Studies on the Reaction of α-Chloroformylarylhydrazine Hydrochloride with Imidazole and 1,2,4-Triazole

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α-Imidazolformylarylhydrazine **2** and α-[1,2,4]triazolformylarylhydrazine **3** have been synthesized through the nucleophilic substitution reaction of **1** with imidazole and 1,2,4-triazole, respectively. 2,2′-Diaryl-2*H*,2′*H*-[4,4′]bi[[1,2,4]-triazolyl]-3,3′-dione **4** was obtained from the cycloaddition of α-chloroformylarylhydrazine hydrochloride **1** with 1,2,4-triazole at 60 ℃ and in absence of n-Bu_3N. The inducing factor for cycloaddition of **1** with 1,2,4-triazole was ascertained as hydrogen ion by the formation of **4** from the reaction of **3** with hydrochloric acid. **4** was also acquired from the reaction of **3** with **1** and this could confirm the reaction route for cycloaddition of **1** with 1,2,4-triazole. Some acylation reagents were applied to induce the cyclization reaction of **2** and **3**. **1** possessing chloroformyl group could induce the cyclization of **2** to give 2-aryl-4-(2-aryl-4-vinyl-semicarbazide-4-yl)-2,4-dihydro-[1,2,4]-triazol-3-one **6**. **7** was obtained from the cyclization of **2** induced by some acyl chlorides. Acetic acid anhydride like acetyl chloride also could react with **2** to produce **7D**. 5-Substituted-3-aryl-3*H*-[1,3,4]oxadiazol-2-one **8** was produced from the cyclization reaction of **3** induced by some acyl chlorides or acetic acid anhydride. The 1,2,4-triazole group of **3** played a role as a leaving group in the course of cyclization reaction. This was confirmed by the same product **8** which was acquired from the reaction of **1**, possessing a better leaving group: Cl, with some acyl chlorides or acetic acid anhydride.

INTRODUCTION

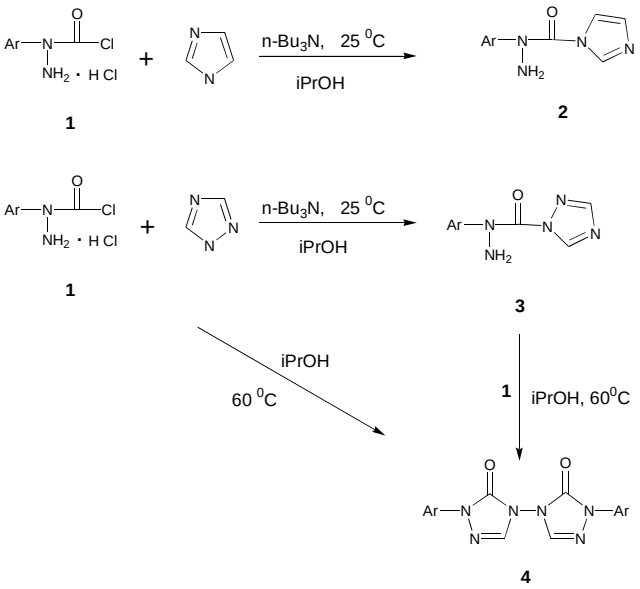
Although α-chloroformylarylhydrazine hydrochloride **1** possesses a chloroformyl group like acyl chloride, its chemical behavior is not the same. Possessing both active amino and chloroformyl groups which occupy advantaged sites for cycloaddition reaction, **1** readily proceeds to intermolecular cycloaddition with itself or some other reagents.[1,2,3,4] The synthetic reactions of some desirable compounds through **1** were often limited to mild conditions. At higher temperature or in more basic conditions, **1** was easily transformed into dimer products.[1] Therefore, successful attempts to undergo a series of derivative reactions from one functional group of **1** often could not be attained.

In our past report,[3,4] many N-heterocyclic compounds reacted with **1** through cycloaddition to obtain the derivates of 2,4-dihydro-1,2,4-triazol-3-one under mildly basic and heating conditions. We thought if some N-heterocyclic compounds possess a second order nitrogen atom which has stronger nucleophility, they can go ahead with nucleophilic substitution reaction but not cycloaddition with **1** under the control of reaction conditions. In this paper, imidazole and 1,2,4-triazole were tried to undergo substitution reaction with **1** since they could react with acyl chloride easily. It was of great interest to introduce a heterocyclic ring into the acyl group of **1** because this work had never been done, and this kind of product was not obtained easily through the other synthetic reaction route. The anticipated products also had not been reported in other papers as yet. This focused our efforts on the study of their derivative reactions.

RESULTS AND DISCUSSION

Imidazole dissolved in iPrOH was stirred with α-chloroformyl arylhydrazine hydrochloride **1** in the presence of n-Bu_3N at room temperature. When the reaction was completed, the major product was isolated and identified as α-imidazolformylarylhydrazine **2** by x-ray spectrum analysis (Fig. 1). Following the same step, 1,2,4-triazole was tested to react with **1**. The product obtained was ascertained as α-[1,2,4]triazolformylarylhydrazine **3** by elemental analysis, ^{1}H NMR and MASS spectrum analysis. The yields of the above two products are shown in Table 1. According to the results of the above two reactions (Scheme I), we found imidazole and 1,2,4-triazole underwent nucleophilic substitution

Scheme I



reaction with **1**.

In one of our previous papers,[4] 3-amino-1,2,4-triazole could proceed to cycloaddition with **1** at 60 °C to obtain 5-amino-bis(2-aryl-2,4-dihydro-1,2,4-triazol-3-on-4-yl). This made us believe that 1,2,4-triazole could also undergo cycloaddition with **1** under some conditions. Therefore, 1,2,4-triazole was attempted to go ahead with cycloaddition with **1** by changing the reaction condition. We found cycloaddition product **4** was isolated from the reaction of **1** with 1,2,4-triazole at 60 ℃ and in the absence of n-Bu_3N (Scheme I), but the yield (Table 2) was low. The structure of **4** was ascertained as 2,2′-diaryl-2*H*,2′*H*-[4,4′]bi[[1,2,4]-triazolyl]-3,3′-dione by elemental analysis, ^{1}H NMR, ^{13}C NMR and MASS spectrum analysis. In order to study the factor inducing the cycloaddition of **1** with 1,2,4-triazole, we designed that compound **3** was tested to undergo intramolecular cyclization under three types of conditions. The first condition was at 60 ℃ and in the presence of n-Bu_3N; the second one was at 60 °C but in the absence of n-Bu_3N; and the third one was at 60 °C and with the addition of concentrated hydrochloric acid. The result (Scheme II) indicated that under the third condition, **5** and **4** were obtained and under the other ones, there was no reaction taking place. **5** was confirmed as 4-amino-2-aryl-2,4-dihydro-3*H*-1,2,4-triazol-3-one by comparing their spectrum in another paper.[5] The reaction route for production of **5** and **4**, we guessed, is shown in Scheme II. According to these results, the factor inducing the cycloaddition of **1** with 1,2,4-triazole was ascertained to be a hydrogen ion. From the poor result for the cycloaddition of **1** with 1,2,4-triazole, we made a guess that as **1** could provide a hydrogen ion itself during the reaction, **1** underwent cycloaddition with 1,2,4-triazole in the absence of n-Bu_3N, but on this acidic condition, the intermediate product **3** was not easily produced, and therefore, the yield of the final product **4** was low. In order to confirm our inference, **3** was tested to react with **1** at 60 ℃ in the absence

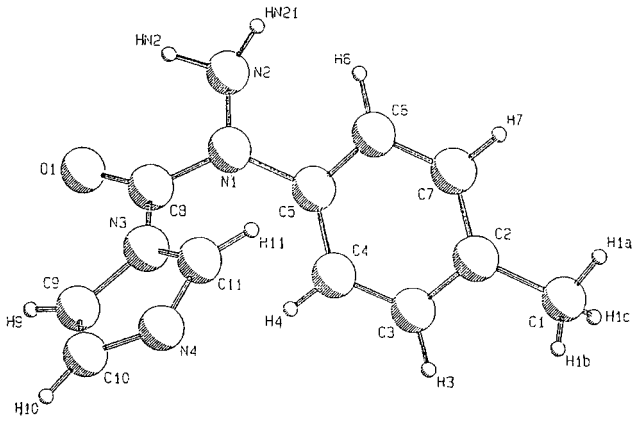


Fig. 1. Molecular Structure of α-Imidazolformyl-4-methylphenyl hydrazine **2c**.

Table 1. The Reactions of **1** with Imidazole (A) and 1,2,4-Triazole (B) at Room Temperature and in the Presence of n-Bu_3N

Product	Ar	Yield	Reagent
2a	C_6H_5	36	A
2b	4-ClC_6H_4	52	A
2c	4-$CH_3C_6H_4$	57	A
3a	C_6H_5	32	B
3b	4-ClC_6H_4	36	B
3c	4-$CH_3C_6H_4$	70	B

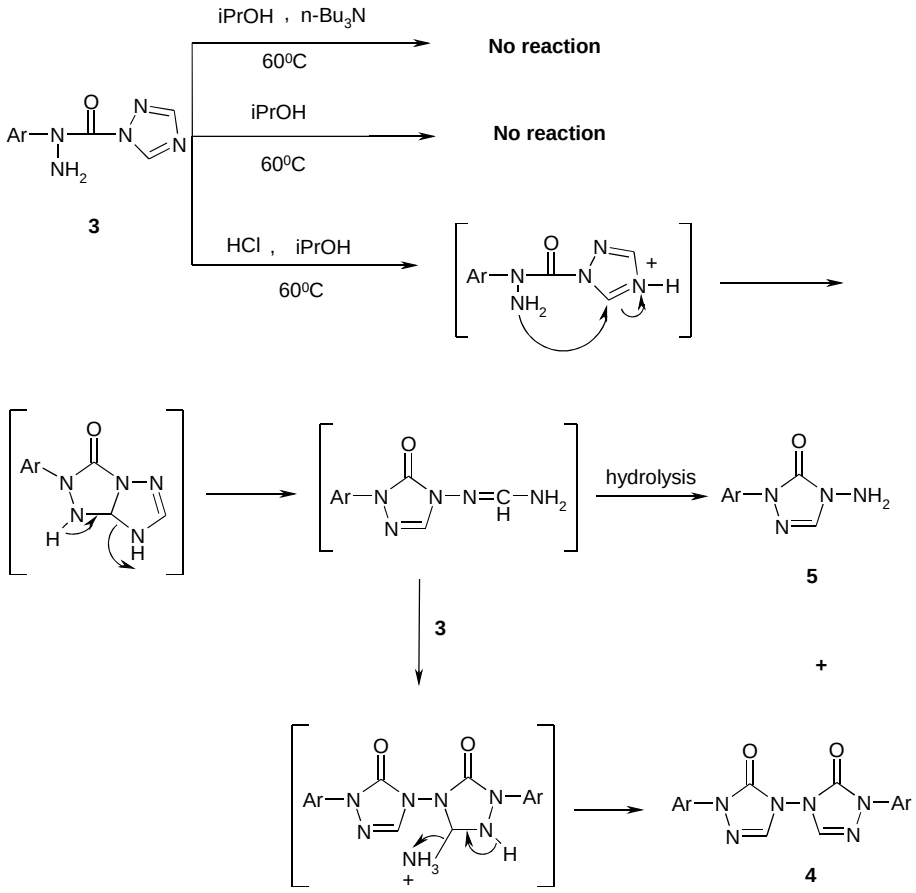
Table 2. The Reaction of **1** with 1,2,4-Triazole at 60 ℃ and in the Absence of n-Bu_3N

Product	Ar	Yield
4aa	C_6H_5	15
4bb	4-ClC_6H_4	13
4cc	4-$CH_3C_6H_4$	18

Table 3. The Reaction of **3** with Hydrochloric Acid at 60 ℃

Product 1	Yield	Product 2	Yield	Ar
4aa	17	**5a**	48	C_6H_5
4bb	14	**5b**	45	4-ClC_6H_4
4cc	19	**5c**	42	4-$CH_3C_6H_4$

Scheme II



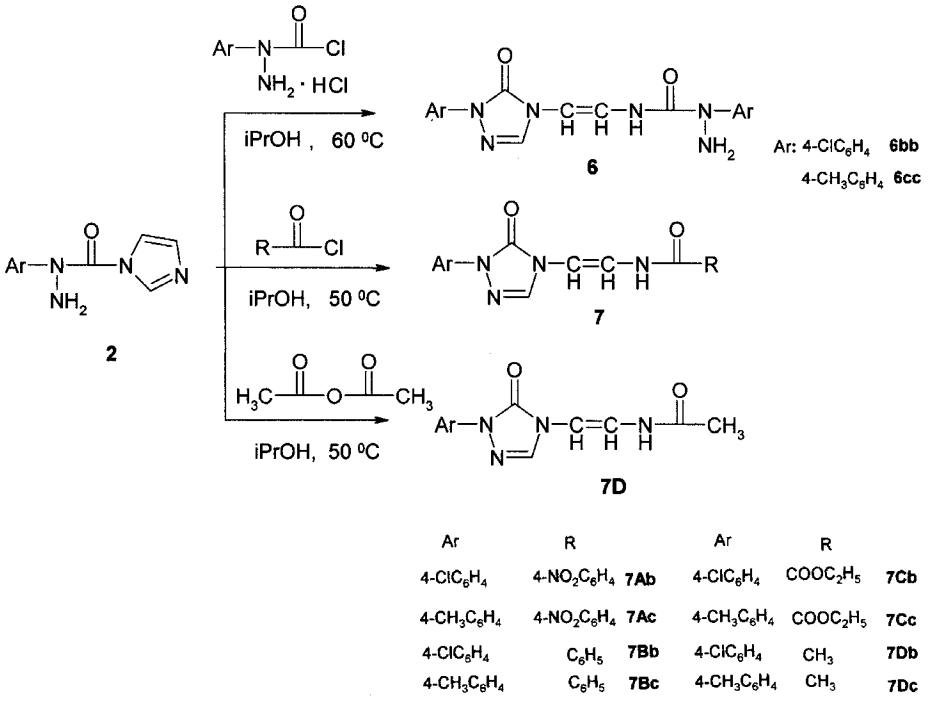
of n-Bu_3N. The product **4** was also acquired and the yield demonstrated in Table 4 was enhanced. This result could ascertain the reaction route in Scheme I.

2 was also attempted to execute intramolecular cyclization by addition of hydrochloric acid, but the anticipated result was not obtained. Another test for the cycloaddition reaction of **2** with **1** was done and 2-aryl-4-(2-aryl-4-vinyl-semicarbazide-4-yl)-2,4-dihydro-[1,2,4]-triazol-3-one **6** was given. According to the structure of **6**, this reaction route could be suggested as that in Scheme III. Investigating this reaction route, we guessed that the factor inducing the cyclization reaction of **2** was the chloroformyl group of **1**. In order to confirm this inference, some acyl chlorides were tested to react with **2**. The results shown in Table 5 indicate that **2** could undergo cyclization reaction induced by acyl chloride to obtain **7**. The structure of **7Db** was identified as

Table 4. The Reaction of **3** with **1** at 60 ℃

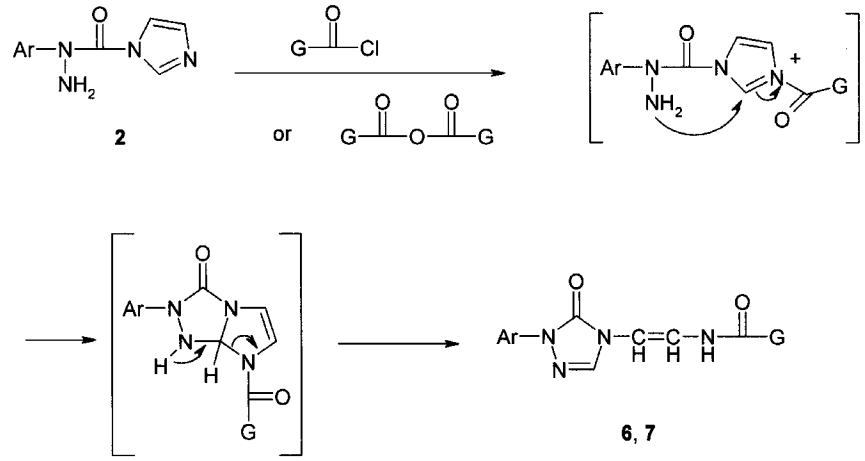
Reactant **3**	Reactant **1**	Product	Ar	Ar	Yield
3a	**1a**	**4aa**	C_6H_5	C_6H_5	46
3a	**1b**	**4ab**	C_6H_5	4-ClC_6H_4	44
3a	**1c**	**4ac**	C_6H_5	4-$CH_3C_6H_4$	48
3b	**1a**	**4ab**	4-ClC_6H_4	C_6H_5	43
3b	**1b**	**4bb**	4-ClC_6H_4	4-ClC_6H_4	42
3b	**1c**	**4bc**	4-ClC_6H_4	4-$CH_3C_6H_4$	45
3c	**1a**	**4ac**	4-$CH_3C_6H_4$	C_6H_5	48
3c	**1b**	**4bc**	4-$CH_3C_6H_4$	4-ClC_6H_4	46
3c	**1c**	**4cc**	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	52

Scheme III



Ar	R		Ar	R	
4-ClC$_6$H$_4$	4-NO$_2$C$_6$H$_4$	7Ab	4-ClC$_6$H$_4$	COOC$_2$H$_5$	7Cb
4-CH$_3$C$_6$H$_4$	4-NO$_2$C$_6$H$_4$	7Ac	4-CH$_3$C$_6$H$_4$	COOC$_2$H$_5$	7Cc
4-ClC$_6$H$_4$	C$_6$H$_5$	7Bb	4-ClC$_6$H$_4$	CH$_3$	7Db
4-CH$_3$C$_6$H$_4$	C$_6$H$_5$	7Bc	4-CH$_3$C$_6$H$_4$	CH$_3$	7Dc

Reaction route:



N-{2-[1-(4-chlorophenyl)-5-oxo-1,5-dihydro-[1,2,4]triazol-4-yl]vinyl}-acetamide (Fig. 2) by x-ray spectrum analysis.

Acetic acid anhydride like acyl chlorides was also tested to react with **2**; we found the product was the same as that obtained from the cyclization reaction induced by acetyl-chloride. According to the above results, we concluded that **2** could undergo intramolecular cyclization induced by some acylation reagents.

Some acylation reagents were also applied to the cyclization of **3** and the product obtained (Table 6) was ascertained as 5-substituted-3-aryl-3*H*-[1,3,4]oxadiazol-2-one **8** by comparing their spectrum in other papers.[1,6,7] This result was different from that obtained through the cyclization reaction of **3** induced by hydrogen ion. According to the structure of **8**, the synthetic reaction route of **8** given from **3** could be shown in Scheme IV and, we thought, the 1,2,4-triazole group of **3** played a role as a leaving group in the course of cyclization reaction. In order to confirm this reaction route, **1**

Table 5. The Reactions of **2** with **1**; 4-Nitrobenzoyl Chloride (**A**); Benzoyl Chloride (**B**); Ethoxalyl Chloride (**C**); Acetyl Chloride (**D**); Ethoxycarbonyl Chloride (**E**) and Acetic Acid Anhydride (**F**)

Reactant **2**	Reagent	Product	Ar	R	Yield
2a	**1a**	**6aa**	C_6H_5		52
2c	**1c**	**6cc**	4-$CH_3C_6H_4$		67
2b	**A**	**7Ab**	4-ClC_6H_4	4-$NO_2C_6H_4$	84
2c	**A**	**7Ac**	4-$CH_3C_6H_4$	4-$NO_2C_6H_4$	81
2b	**B**	**7Bb**	4-ClC_6H_4	C_6H_5	82
2c	**B**	**7Bc**	4-$CH_3C_6H_4$	C_6H_5	83
2b	**C**	**7Cb**	4-ClC_6H_4	$COOC_2H_5$	76
2c	**C**	**7Cc**	4-$CH_3C_6H_4$	$COOC_2H_5$	72
2b	**D**	**7Db**	4-ClC_6H_4	CH_3	73
2c	**D**	**7Dc**	4-$CH_3C_6H_4$	CH_3	63
2b	**E**	**7Eb**	4-ClC_6H_4	OC_2H_5	55
2c	**E**	**7Ec**	4-$CH_3C_6H_4$	OC_2H_5	36
2b	**F**	**7Db**	4-ClC_6H_4	CH_3	73
2c	**F**	**7Dc**	4-$CH_3C_6H_4$	CH_3	66

Table 6. The Reactions of **3** with 4-Nitrobenzoyl Chloride (**A**); Benzoyl Chloride (**B**); Ethoxalyl Chloride (**C**); Acetyl Chloride (**D**) and Acetic Acid Anhydride (**E**)

Reactant	Reagent	Product	Ar	R	Yield
3c	**A**	**8Ac**	4-$CH_3C_6H_5$	4-$NO_2C_6H_4$	52
3c	**B**	**8Bc**	4-$CH_3C_6H_4$	C_6H_5	67
3c	**C**	**8Cc**	4-$CH_3C_6H_4$	$COOC_2H_5$	84
3c	**D**	**8Dc**	4-$CH_3C_6H_4$	CH_3	81
3c	**E**	**8Dc**	4-$CH_3C_6H_4$	CH_3	82

possessing a better leaving group: Cl was tested to react with acyl chlorides or acetic acid anhydride. The product **8** was also obtained and the yield is shown in Table 7.

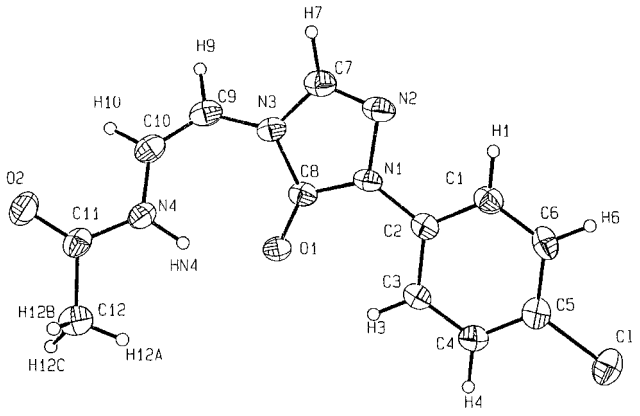


Fig. 2. Molecular Structure of N-{2-[1-(4-Chlorophenyl)-5-oxo-1,5-dihydro-[1,2,4]triazol-4-yl] vinyl}acetamide **7Db**.

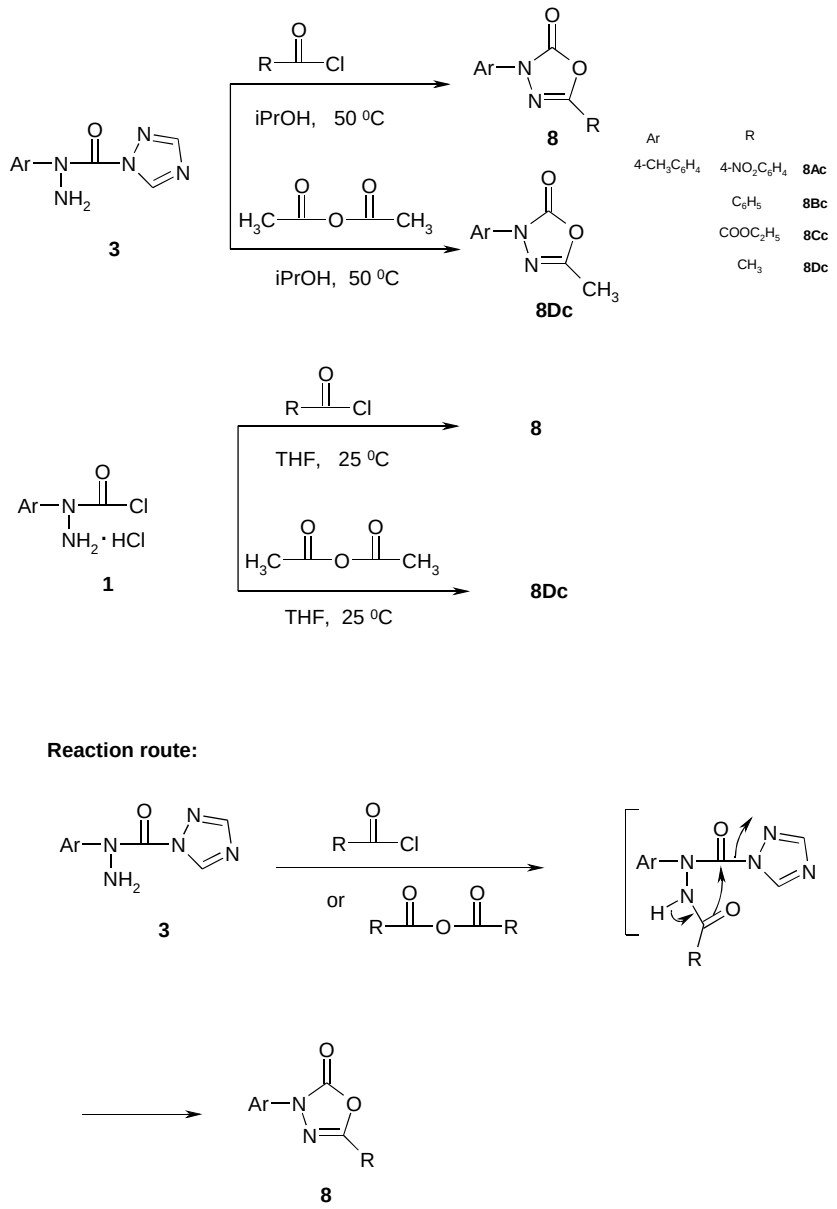
CONCLUSION

2 and **3** have been synthesized through the nucleophilic substitution reaction of **1** with imidazole and 1,2,4-triazole, respectively. **4** was obtained from the cycloaddition of **1** with 1,2,4-triazole at 60 °C and in the absence of n-Bu_3N. The inducing factor for cycloaddition of **1** with 1,2,4-triazole was ascertained as hydrogen ion by the formation of **4** from the reaction of **3** with hydrochloric acid. **4** was also acquired from the reaction of **3** with **1** and this could confirm the reaction route for cycloaddition of **1** with 1,2,4-triazole.

Some acylation reagents were applied to induce the cyclization reaction of **2** and **3**. **1** possessing chloroformyl group could induce the cyclization of **2** to give **6**. **7** was obtained from the cyclization of **2** induced by some acyl chlorides. Acetic acid anhydride like acetyl chloride also could react with **2** to produce **7D**.

The result from the cyclization reaction of **3** induced by some acylation reagents was different from that induced by hydrogen ion. Some acyl chlorides or acetic acid anhydride

Scheme IV



could react with **3** to obtain **8**. The 1,2,4-triazole group of **3** played a role as a leaving group in the course of cyclization reaction. This was confirmed by the same product **8** which was acquired from the reaction of **1**, possessing a better leaving group: Cl, with some acyl chlorides or acetic acid anhydride.

EXPERIMENTAL SECTION

General

Melting points (Buchi 535 apparatus) are uncorrected. IR spectra were recorded on a Hitachi 270-30 infrared spectro-photometer. NMR spectra were measured on a Bruker AMX-200 NMR spectrometer with tetramethylsilane as internal standard. The mass spectra were registered on a Finnigan MAT TSQ-46C spectrometer at an ionizing potential of 70 eV. Elemental analyses were performed on Heraeus CHN-O-Rapid and Tacussel Coulomax 78 analyzers. X-ray analyses were made with a Nonius CAD-4 diffractometer. Column chromatography was carried out on silica gel (Kieselgel 100, 70-230 mesh, E. Merck).

Synthesis of 2 from the reaction of 1 with imidazole

Imidazole (0.34 g, 5 mmol) dissolved in iPrOH was

Table 7. The Reactions of **1** with 4-Nitrobenzoyl Chloride (**A**); Benzoyl Chloride (**B**); Ethoxalyl Chloride (**C**); Acetyl Chloride (**D**) and Acetic Acid Anhydride (**E**)

Reactant	Reagent	Product	Ar	R	Yield
1c	**A**	**8Ac**	4-$CH_3C_6H_5$	4-$NO_2C_6H_4$	62
1c	**B**	**8Bc**	4-$CH_3C_6H_4$	C_6H_5	79
1c	**C**	**8Cc**	4-$CH_3C_6H_4$	$COOC_2H_5$	80
1c	**D**	**8Dc**	4-$CH_3C_6H_4$	CH_3	70
1c	**E**	**8Dc**	4-$CH_3C_6H_4$	CH_3	72

Table 8. Crystal Data for **2c**, **7Db**

Compound	**2c**	**7Db**
Formula	$C_{11}H_{12}N_4O$	$C_{12}H_{11}ClN_4O_2$
fw	216.24	288.42
cryst system	Triclinic	Triclinic
space group	P-1	P-1
a, Å	11.6071(9)	4.2449(24)
b, Å	5.6841(8)	12.700(5)
c, Å	16.6714(11)	23.933(3)
α, deg	90.000(11)	100.333(21)
β, deg	103.344(10)	95.080(22)
γ, deg	89.960(9)	99.54(3)
V, $Å^3$	1070.22(19)	1242.4(9)
Z	2	2
D_{calcd}, g cm^{-3}	1.342	1.49
λ(Mo-Kα), Å	0.70930	0.70930
F_{000}	456.18	595.00
Range, deg	24, 9.84-34.66	24, 12.60-28.26
$2\theta_{max}$,deg	49.9	44.9
scan type	θ-2θ	θ-2θ
μ/cm^{-1}	0.09	0.31
Reflections measured	2202	3435
Unique reflections	2183	3257
Observed reflections	1029	1827
Refined parameters	249	343
R_f for significant reflections	0.079	0.051
R_w for significant reflections	0.083	0.051
GOF	3.02	2.16

stirred with **1a** (0.517 g, 2.56 mmol) and n-Bu_3N (1.5 g) at room temperature for 2 hours. After the reaction, iPrOH was removed from the reaction mixture and the residue was subjected to column separation (eluent: EtOAc/n-hexane = 4:1) to give **2a**. According to this procedure, the reactions of **1b** and**1c** with imidazole were undergone, but there was precipitate produced in the reaction mixture. The precipitate was filtered and then recrystalized from EtOAc + iPrOH to give **2b**, **2c**.

α-Imidazolformylphenyl hydrazine 2a

mp 99-100 °C; IR (KBr) 3316, 3178, 1680 cm^{-1}; ^1H

Table 9. Bond Distances/Å of **2c**

C(1)-C(2)	1.514(14)	C(8)-O(1)	1.202(11)
C(1)-H(1a)	0.955	C(8)-N(1)	1.354(12)
C(1)-H(1b)	0.938	C(8)-N(3)	1.426(14)
C(1)-H(1c)	0.945	C(9)-C(10)	1.270(15)
C(2)-C(3)	1.370(21)	C(9)-N(3)	1.378(12)
C(2)-C(7)	1.359(24)	C(9)-H(9)	0.962
C(3)-C(4)	1.380(13)	C(10)-N(4)	1.369(16)
C(3)-H(3)	0.967	C(10)-H(10)	0.958
C(4)-C(5)	1.358(22)	C(11)-N(3)	1.399(14)
C(4)-H(4)	0.952	C(11)-N(4)	1.361(16)
C(5)-C(6)	1.387(18)	C(11)-H(11)	0.952
C(5)-N(1)	1.449(11)	N(1)-N(2)	1.435(10)
C(6)-C(7)	1.366(14)	N(2)-H(n2)	0.957
C(6)-H(6)	0.975	N(2)-H(n21)	0.961
C(7)-H(7)	0.963		

Table 10. Bond Angles/deg of **2c**

C(2)-C(1)-H(1a)	110.8	C(6)-C(7)-H(7)	120.9
C(2)-C(1)-H(1b)	111.3	O(1)-C(8)-N(1)	125.2(10)
C(2)-C(1)-H(1c)	109.9	O(1)-C(8)-N(3)	118.2(9)
H(1a)-C(1)-H(1b)	108.6	N(1)-C(8)-N(3)	116.6(8)
H(1a)-C(1)-H(1c)	107.8	C(10)-C(9)-N(3)	112.0(9)
H(1b)-C(1)-H(1c)	108.5	C(10)-C(9)-H(9)	125.8
C(1)-C(2)-C(3)	119.4(15)	N(3)-C(9)-H(9)	122.1
C(1)-C(2)-C(7)	122.8(14)	C(9)-C(10)-N(4)	107.2(9)
C(3)-C(2)-C(7)	117.8(10)	C(9)-C(10)-H(10)	128.2
C(2)-C(3)-C(4)	121.9(15)	N(4)-C(10)-H(10)	124.4
C(2)-C(3)-H(3)	119.7	N(3)-C(11)-N(4)	105.0(10)
C(4)-C(3)-H(3)	118.1	N(3)-C(11)-H(11)	127.9
C(3)-C(4)-C(5)	119.0(13)	N(4)-C(11)-H(11)	127.1
C(3)-C(4)-H(4)	124.5	C(5)-N(1)-C(8)	126.0(8)
C(5)-C(4)-H(4)	116.5	C(5)-N(1)-N(2)	117.9(7)
C(4)-C(5)-C(6)	120.2(9)	C(8)-N(1)-N(2)	115.5(6)
C(4)-C(5)-N(1)	121.3(11)	N(1)-N(2)-H(n2)	109.6
C(6)-C(5)-N(1)	118.5(13)	N(1)-N(2)-H(n21)	109.8
C(5)-C(6)-C(7)	119.0(14)	H(n2)-N(2)-H(n21)	108.0
C(5)-C(6)-H(6)	120.2	C(8)-N(3)-C(9)	121.8(9)
C(7)-C(6)-H(6)	120.7	C(8)-N(3)-C(11)	132.5(9)
C(2)-C(7)-C(6)	122.1(13)	C(9)-N(3)-C(11)	105.7(8)
C(2)-C(7)-H(7)	117.0	C(10)-N(4)-C(11)	110.1(10)

Table 11. Bond Distances/Å of **7Db**

C(1)-C(2)	1.366(8)	C(8)-N(1)	1.359(8)
C(1)-C(6)	1.385(10)	C(8)-N(3)	1.397(8)
C(1)-H(1)	0.961	C(9)-C(10)	1.311(10)
C(2)-C(3)	1.384(9)	C(9)-N(3)	1.394(9)
C(2)-N(1)	1.425(8)	C(9)-H(9)	0.953
C(3)-C(4)	1.367(9)	C(10)-N(4)	1.394(9)
C(3)-H(3)	0.957	C(10)-H(10)	0.947
C(4)-C(5)	1.356(9)	C(11)-C(12)	1.506(10)
C(4)-H(4)	0.981	C(11)-O(2)	1.207(8)
C(5)-C(6)	1.380(10)	C(11)-N(4)	1.353(9)
C(5)-C(1)	1.733(6)	C(12)-H(12a)	0.954(6)
C(6)-H(6)	0.941	C(12)-H(12b)	0.961(7)
C(7)-N(2)	1.273(9)	C(12)-H(12c)	0.941(6)
C(7)-N(3)	1.355(8)	N(1)-N(2)	1.389(7)
C(7)-H(7)	0.978(7)	N(4)-H(n4)	0.952
C(8)-O(1)	1.224(8)		

Table 12. Bond Angles/deg of **7Db**

C(2)-C(1)-C(6)	120.1(6)	C(10)-C(9)-H(9)	114.2
C(2)-C(1)-H(1)	119.9	N(3)-C(9)-H(9)	116.1
C(6)-C(1)-H(1)	120.0	C(9)-C(10)-N(4)	127.5(6)
C(1)-C(2)-C(3)	120.2(6)	C(9)-C(10)-H(10)	116.7
C(1)-C(2)-N(1)	118.8(5)	N(4)-C(10)-H(10)	115.8
C(3)-C(2)-N(1)	121.0(5)	C(12)-C(11)-O(2)	121.5(6)
C(2)-C(3)-C(4)	119.2(5)	C(12)-C(11)-N(4)	115.3(6)
C(2)-C(3)-H(3)	120.1	O(2)-C(11)-N(4)	123.3(6)
C(4)-C(3)-H(3)	120.7	C(11)-C(12)-H(12a)	111.6
C(3)-C(4)-C(5)	121.0(6)	C(11)-C(12)-H(12b)	110.8
C(3)-C(4)-H(4)	119.9	C(11)-C(12)-H(12c)	111.8
C(5)-C(4)-H(4)	119.1	H(12a)-C(12)-H(12b)	105.9
C(4)-C(5)-C(6)	120.3(6)	H(12a)-C(12)-H(12c)	107.7
C(4)-C(5)-C(1)	120.7(5)	H(12b)-C(12)-H(12c)	108.9
C(6)-C(5)-C(1)	119.0(5)	C(2)-N(1)-C(8)	128.8(5)
C(1)-C(6)-C(5)	119.1(5)	C(2)-N(1)-N(2)	118.6(5)
C(1)-C(6)-H(6)	120.8	C(8)-N(1)-N(2)	112.4(5)
C(5)-C(6)-H(6)	120.1	C(7)-N(2)-N(1)	103.0(5)
N(2)-C(7)-N(3)	115.2(6)	C(7)-N(3)-C(8)	105.7(5)
N(2)-C(7)-H(7)	121.6	C(7)-N(3)-C(9)	125.4(5)
N(3)-C(7)-H(7)	123.2	C(8)-N(3)-C(9)	128.8(5)
O(1)-C(8)-N(1)	129.8(6)	C(10)-N(4)-C(11)	121.2(5)
O(1)-C(8)-N(3)	126.5(6)	C(10)-N(4)-H(n4)	117.5
N(1)-C(8)-N(3)	103.7(5)	C(11)-N(4)-H(n4)	121.3
C(10)-C(9)-N(3)	129.6(6)		

NMR (DMSO-d_6) δ 8.35 (s, 1H), 7.63 (d, J = 2.1 Hz, 1H), 7.21-7.62 (m, 5H), 6.94 (d, J = 2.1 Hz, 1H), 5.7 (s, 2H); EIMS (70 eV) *m/z*: 202 (M^+, 100), 175 (84), 135 (69), 119 (51), 107 (90), 77 (86), 68 (40), 64 (28). Anal. Calcd for $C_{10}H_{10}N_4O$: C, 59.41; H, 4.95; N, 27.72. Found: C, 59.64; H, 5.01; N, 27.56.

α-Imidazolformyl-4-chlorophenyl hydrazine 2b

mp 115-116 °C; IR (KBr) 3364, 3280, 3172, 1680 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 8.38 (s, 1H), 7.68 (d, J = 2.2 Hz, 1H), 7.58 (d, J = 9.0 Hz, 2H), 7.46 (d, J = 9.0 Hz, 2H), 6.96 (d, J = 2.2 Hz, 1H), 5.71 (s, 2H); EIMS (70 eV) *m/z*: 238 (M^++2, 31), 236 (M^+, 72), 209 (46), 169 (26), 153 (57), 141 (96), 77 (100), 68 (72), 63 (33). Anal. Calcd for $C_{10}H_{10}ClN_4O$: C, 50.75; H, 3.83; N, 23.67; Cl, 14.98. Found: C, 50.64; H, 3.89; N, 23.63; Cl, 15.00.

α-Imidazolformyl-4-methylphenyl hydrazine 2c

mp 135-136 °C; IR (KBr) 3334, 3292, 3190, 3136, 1725, 1692 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 8.32 (s, 1H), 7.60 (d, J = 0.8 Hz, 1H), 7.39 (d, J = 8.5 Hz, 2H), 7.19 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 0.8 Hz, 1H), 5.63 (s, 2H), 2.31 (s, 3H); EIMS (70 eV) *m/z*: 216 (M^+, 100), 189 (12), 149 (13), 133 (20), 121 (57), 77 (45), 68 (72), 63 (10). Anal. Calcd for $C_{11}H_{12}N_4O$: C, 61.11; H, 5.56; N, 25.93. Found: C, 61.19; H, 5.50; N, 25.73.

Synthesis of 3 from the reaction of 1 with 1,2,4-triazole

1,2,4-Triazole (0.69 g, 10 mmol) dissolved in iPrOH was stirred with **1a** (0.517 g, 2.56 mmol) and n-Bu_3N (1.5 g) at room temperature for 2 hours. After the reaction, iPrOH was removed from the reaction mixture and the residue was subjected to column separation (eluent: EtOAc/n-hexane = 6:1) to give **3a**. According to this procedure, the reactions of various **1** with 1,2,4-triazole were achieved.

α-[1,2,4]-triazolformylphenylhydrazine 3a

mp 124-125 °C; IR (KBr) 3352, 3220, 3166, 3106, 1695 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 9.14 (s, 1H), 8.12 (s, 1H), 7.20-7.49 (m, 5H), 5.75 (s, 2H); EIMS (70 eV) *m/z*: 203 (M^+, 47), 146 (67), 107 (59), 91 (23), 77 (100), 70 (60), 64 (17). Anal. Calcd for $C_9H_9N_5O$: C, 53.20; H, 4.43; N, 34.48. Found: C, 53.24; H, 4.37; N, 34.69.

α-[1,2,4]-triazolformyl-4-chlorophenylhydrazine 3b

mp 141-142 °C; IR (KBr) 3304, 3238, 3184, 3130, 1740, 1704 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 9.17 (s, 1H), 8.14 (s, 1H), 7.48 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 5.78 (s, 2H); EIMS (70 eV) *m/z*: 239 (M^++2, 10), 237 (M^+, 36), 180 (92), 141 (83), 111 (47), 77 (100), 70 (77). Anal. Calcd for $C_9H_8ClN_5O$: C, 45.57; H, 3.38; N, 29.54; Cl, 14.77. Found: C, 45.65; H, 3.43; N, 29.48; Cl, 14.84.

α-[1,2,4]-triazolformyl-4-methylphenylhydrazine 3c

mp 161-162 °C; IR (KBr) 3340, 3220, 3172, 3106, 1680 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 9.11 (s, 1H), 8.11 (s, 1H), 7.35 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 8.3 Hz, 2H), 5.69 (s, 2H), 2.29 (s, 3H); EIMS (70 eV) *m/z*: 217 (M^+, 73), 160 (100), 121 (91), 91 (95), 77 (47), 70 (27). Anal. Calcd for $C_{10}H_{11}N_5O$: C,

55.30; H, 5.07; N, 32.26. Found: C, 55.25; H, 4.89; N, 32.09.

The reaction of 1 with 1,2,4-triazole in the absence of n-Bu_3N

[1,2,4]-Triazole (0.86 g, 12.5 mmol) dissolved in iPrOH (10 mL) was stirred with **1a** (0.517 g, 2.56 mmol) at 60 ℃ for thirty minutes. After the reaction, the white precipitate was filtered to obtain **4aa**. According to this procedure, the reactions of various **1** with 1,2,4-triazole were achieved.

2,2′-Diphenyl-2*H*,2′*H*-[4,4′]bi[[1,2,4]-triazolyl]-3,3′-dione (4aa)

mp > 250 ℃; IR (KBr) 3142, 3088, 1728, 1704 cm^{-1}; ^1H NMR (DMSO-d_6)) δ 8.80 (s, 2H), 7.33-7.86 (m, 10H); ^{13}C NMR (DMSO-d_6)) δ 147.85, 137.15, 136.91, 129.48, 126.31, 118.31; EIMS (70 eV) *m/z*: 321 (M^++1, 18), 320 (M^+, 85), 260 (31), 132 (12), 119 (13),104 (22), 91 (32), 77 (100), 64 (13). Anal. Calcd for $C_{16}H_{12}N_6O_2$: C, 60.00; H, 3.78; N, 26.24. Found: C, 59.87; H, 3.69; N, 26.18.

2,2′-Bis(4-chlorophenyl)-2*H*,2′*H*-[4,4′]bi[[1,2,4]-triazolyl]-3,3′-dione (4bb)

mp > 250 ℃; IR (KBr) 3130, 3082, 1728, 1704 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.79 (s, 2H), 7.89 (d, *J* = 8.9 Hz, 4H), 7.59 (d, *J* = 8.9 Hz, 4H); ^{13}C NMR (DMSO-d_6) δ 147.81, 135.78, 131.54, 129.01, 127.11, 118.34; EIMS (70 eV) *m/z*: 392 (M^++4, 10) 390 (M^++2, 15), 388 (M^+, 22), 194 (25), 138 (25), 125 (28), 111 (100), 89 (29), 75 (37), 63 (21). Anal. Calcd for $C_{16}H_{10}C_{l2}N_6O_2$: C, 49.38; H, 2.59; N, 21.59; Cl, 18.22. Found: C, 49.20; H, 2.50; N, 21.48; Cl, 18.00.

2,2′-Di-p-tolyl-2*H*,2′*H*-[4,4′]bi[[1,2,4]-triazolyl]-3,3′-dione (4cc)

mp > 250 ℃; IR (KBr) 3136, 3088, 1728, 1704, 1515, 1386 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.77 (s, 2H), 7.76 (d, *J* = 8.6 Hz, 4H), 7.35 (d, *J* = 8.6 Hz, 4H), 2.34 (s, 6H); ^{13}C NMR (DMSO-d_6) δ 147.77, 136.93, 135.63, 134.56, 129.82, 118.35, 20.54; EIMS (70 eV) *m/z*: 349 (M^++1, 22), 348 (M^+, 100), 174 (27), 146 (8), 132 (8), 118 (12), 105 (12), 91 (51), 73 (10), 65 (12). Anal. Calcd for $C_{18}H_{16}N_6O_2$: C, 62.06; H, 4.63; N, 24.12. Found: C, 62.00; H, 4.58; N, 23.98.

The reaction of 3 with hydrochloric acid

3c (0.217 g, 1 mmol) dissolved in iPrOH (8 mL) was stirred with concentrated hydrochloric acid (5 mL) at 60 ℃ for 2 hours. After the reaction, the precipitate was filtered to obtain **4c**. iPrOH was removed from the filtrate and the residue was subjected to column separation (eluent: EtOAc/n-hexane = 3:2) to give **5c**. According to this procedure, the reactions of various **3** with hydrochloric acid were achieved.

4-Amino-2-phenyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one 5a

mp 161-162 ℃; IR (KBr) 3322, 3280, 3214, 1716 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.23 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.45 (t, *J* = 8.4 Hz, 2H), 7.22 (t, *J* = 8.4 Hz, 1H), 5.55 (s, 2H); FABMS *m/z*: 177 (M^++1, 100), 176 (M^+, 52), 136 (19). Anal. Calcd for $C_8H_8N_4O$: C, 54.54; H, 4.58; N, 31.80. Found: C, 54.58; H, 4.65; N, 31.78.

4-Amino-2-(4-chlorophenyl)-2,4-dihydro-3*H*-1,2,4-triazol-3-one 5b

mp 184-185 ℃; IR (KBr) 3334, 3226, 1710 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.26 (s, 1H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 5.55 (s, 2H); FABMS *m/z*: 211 (M^++1, 100), 210 (M^+, 62). Anal. Calcd for $C_8H_7ClN_4O$: C, 45.62; H, 3.35; N, 26.60. Found: C, 45.53; H, 3.35; N, 26.66.

4-Amino-2-(4-methylphenyl)-2,4-dihydro-3*H*-1,2,4-triazol-3-one 5c

mp 163-164 ℃; IR (KBr) 3340, 3298, 3232, 1698 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.19 (s, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 5.52 (s, 2H), 2.29 (s, 3H); FABMS *m/z*: 191 (M^++1, 100), 190 (M^+, 66), 154 (19). Anal. Calcd for $C_9H_{10}N_4O$: C, 56.83; H, 5.30; N, 29.50. Found: C, 56.83; H, 5.37; N, 29.63.

The reaction of 3 with 1

3a (0.203 g, 1 mmol) dissolved in iPrOH (10 mL) was stirred with **1a** (0.207 g, 1 mmol) at 60 ℃ for 30 minutes. After the reaction, the precipitate was filtered to obtain **4aa**. According to this procedure, the reactions of various **3** with various **1** were achieved.

2-Phenyl-2′-(4-chlorophenyl)-2*H*,2′*H*-[4,4′]bi[[1,2,4]-triazolyl]-3,3′-dione (4ab)

mp > 250 ℃; IR (KBr) 3136, 3088, 1728, 1704 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.82 (s, 1H), 8.81 (s, 1H), 7.29-7.93 (m, 9H); EIMS (70 eV) *m/z*: 356 (M^++2, 32), 354 (M^+, 100), 320 (37), 194 (17), 160 (25),125 (11), 111 (25), 91 (24), 77 (63), 63 (9). Anal. Calcd for $C_{16}H_{11}ClN_6O_2$: C, 54.17; H, 3.13; N, 23.69; Cl, 9.99. Found: C, 54.01; H, 3.03; N, 23.41; Cl, 9.84.

2-Phenyl-2′-p-tolyl-2*H*,2′*H*-[4,4′]bi[[1,2,4]-triazolyl]-3,3′-dione (4ac)

mp > 250 ℃; IR (KBr) 3133, 3084, 1730, 1704 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.80 (s, 1H), 8.77 (s, 1H), 7.89 (d, *J* = 8.8

Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.54 (t, *J* = 8.8 Hz, 2H), 7.33 (m, 3H), 2.3 (s, 3H); EIMS (70 eV) *m/z*: 335 (M^++1, 22), 334 (M^+, 100), 174 (33), 160 (25), 105 (11), 91 (33), 77 (65). Anal. Calcd for $C_{17}H_{14}N_6O_2$: C, 61.07; H, 4.22; N, 25.14. Found: C, 60.98; H, 4.20; N, 25.09.

2-(4-Chlorophenyl)-2′-p-tolyl-2*H*,2′*H*-[4,4′]bi[[1,2,4]-triazolyl]-3,3′-dione (4bc)

mp > 250 ℃; IR (KBr) 3448, 3136, 3084, 1726, 1707 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.79 (s, 1H), 8.76 (s, 1H), 7.89 (d, *J* = 8.9 Hz, 2H), 7.75 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.9 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 2.3 (s, 3H); EIMS (70 eV) *m/z*: 370 (M^++2, 33), 368 (M^+, 100), 348 (82), 194 (7), 174 (38),146 (17), 111 (26), 91 (90), 65 (17). Anal. Calcd for $C_{17}H_{13}ClN_6O_2$: C, 55.37; H, 3.55; N, 22.79; Cl, 9.61. Found: C, 55.24; H, 3.45; N, 22.63; Cl, 9.52.

The reaction of 2 with 1

2a (0.202 g, 1 mmol) was dissolved in iPrOH (10 mL) and then stirred with **1a** (0.517 g, 2.5 mmol) at 60 ℃ for 30 minutes. After the reaction, iPrOH was removed from the reaction mixture and the residue was subjected to column separation (eluent: EtOAc/n-hexane = 1:3) to give **6aa**. According to this procedure, the reaction of **2c** with **1c** was achieved.

2-Phenyl-4-(2-phenyl-4-vinylsemicarbazide-4-yl)-2,4-dihydro-[1,2,4]triazol-3-one 6aa

mp 193-194 °C; IR (KBr) 3328, 3262, 3208, 3100, 2926, 1713, 1692, 1656 cm^{-1}; ^1H NMR (DMSO-d_6) δ 10.11 (d, *J* = 10.8 Hz, 1H), 8.34 (s, 1H), 7.87-7.08 (m, 10H), 6.63 (dd, *J* = 10.8, 7.4 Hz, 1H), 5.78 (d, *J* = 7.4 Hz, 1H), 5.44 (s, 2H); EIMS (70 eV) *m/z*: 336 (M^+, 6), 293 (48), 229 (43), 161 (19), 133 (19), 119 (23), 108 (100), 91 (62), 77 (92), 65 (33). Anal. Calcd for $C_{17}H_{16}N_6O_2$: C, 60.70; H, 4.80; N, 25.00. Found: C, 60.73; H, 4.86; N, 24.88.

2-(4-Methylphenyl)-4-(2-(4-methylphenyl)-4-vinylsemicarbazide-4-yl)-2,4-dihydro-[1,2,4]triazol-3-one 6cc

mp 213-214 °C; IR (KBr) 3328, 3274, 3208, 3100, 2920, 1713, 1692, 1653, 1635 cm^{-1}; ^1H NMR (DMSO-d_6) δ 10.07 (d, *J* = 10.8 Hz, 1H), 8.31 (s, 1H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.63 (dd, *J* = 10.8, 7.4 Hz, 1H), 5.76 (d, *J* = 7.4 Hz, 1H), 5.34 (s, 2H), 2.32 (s, 3H), 2.26 (s, 3H); EIMS (70 eV) *m/z*: 364 (M^+, 6), 321 (16), 243 (41), 175 (14), 133 (13), 122 (100), 105 (27), 91 (41), 77 (20), 65 (12). Anal. Calcd for $C_{19}H_{20}N_6O_2$: C, 62.65; H, 5.50; N, 23.10. Found: C, 62.43; H, 5.44; N, 22.82.

The reaction of 2 with acyl chloride or acetic acid anhydride

2 (1 mmol) dissolved in iPrOH (10 mL) was stirred with various acyl chlorides or acetic acid anhydride (2 mmol) at 50 °C for 2 hours. After the reaction, if there was precipitate produced in the reaction mixture, the precipitate was filtered to obtain **7**; if there was no precipitate in the reaction mixture, iPrOH was removed from the filtrate and the residue was subjected to column separation (eluent: EtOAc/n-hexane = 1:3) to give **7**.

N-{2-[1-(4-Chlorophenyl)-5-oxo-1,5-dihydro-[1,2,4]triazol-4-yl]vinyl}-4-nitrobenzamide 7Ab

mp 249-250 ℃; IR (KBr) 3112, 1713, 1680, 1605 cm^{-1}; ^1H NMR (DMSO-d_6) δ 10.71 (d, *J* = 10.0 Hz, 1H), 8.45 (s, 1H), 8.37 (d, *J* = 8.9 Hz, 2H), 8.12 (d, *J* = 8.9 Hz, 2H), 7.95 (d, *J* = 8.9 Hz, 2H), 7.56 (d, *J* = 8.9 Hz, 2H), 6.98 (dd, *J* = 10.0, 7.2 Hz, 1H), 6.00 (d, *J* = 7.2 Hz, 1H); EIMS (70 eV) *m/z*: 387 (M^++2, 11), 385 (M^+, 32), 150 (100), 120 (9), 104 (27), 76 (10). Anal. Calcd for $C_{17}H_{12}ClN_5O_4$: C, 52.99; H, 3.12; N, 18.18; Cl, 9.09. Found: C, 52.88; H, 3.25; N, 18.06; Cl, 9.14.

N-{2-[1-(4-Methylphenyl)-5-oxo-1,5-dihydro-[1,2,4]triazol-4-yl]vinyl}-4-nitrobenzamide 7Ac

mp 189-190 ℃; IR (KBr) 3094, 1710, 1671, 1605 cm^{-1}; ^1H NMR (DMSO-d_6) δ 10.86 (d, *J* = 10.1 Hz, 1H), 8.40 (s, 1H), 8.36 (d, *J* = 8.5 Hz, 2H), 8.11 (d, *J* = 8.5 Hz, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 6.93 (dd, *J* = 10.1, 7.3 Hz, 1H), 6.02 (d, *J* = 7.3 Hz, 1H); EIMS (70 eV) *m/z*: 366 (M^++1, 16), 365 (M^+, 84), 336 (11), 263 (32), 175 (20), 150 (100), 133 (28), 120 (29), 104 (63), 91 (33), 76 (34), 65 (19). Anal. Calcd for $C_{18}H_{15}N_5O_4$: C, 59.18; H, 4.11; N, 19.18. Found: C, 59.07; H, 4.21; N, 19.04.

N-{2-[1-(4-Chlorophenyl)-5-oxo-1,5-dihydro-[1,2,4]triazol-4-yl]vinyl}benzamide 7Bb

mp 206-207 ℃; IR (KBr) 3166, 3088, 1713, 1680, 1659 cm^{-1}; ^1H NMR (DMSO-d_6) δ 10.50 (d, *J* = 10.1 Hz, 1H), 8.41 (s, 1H), 7.91-7.57 (m, 9H), 6.97 (dd, *J* = 10.1, 7.3 Hz, 1H), 5.93 (d, *J* = 7.3 Hz, 1H); EIMS (70 eV) *m/z*: 342 (M^++2, 8), 340 (M^+, 23), 153 (5), 125 (7), 105 (100), 77 (53). Anal. Calcd for $C_{17}H_{13}ClN_4O_2$: C, 60.00; H, 3.82; N, 16.47; Cl, 10.3. Found: C, 59.90; H, 3.82; N, 16.41; Cl, 10.40.

N-{2-[1-(4-Methylphenyl)-5-oxo-1,5-dihydro-[1,2,4]triazol-4-yl]vinyl}benzamide 7Bc

mp 199-200 ℃; IR (KBr) 3424, 3148, 3088, 2962, 1713, 1674, 1605 cm^{-1}; ^1H NMR (DMSO-d_6) δ 10.68 (d, *J* =

10.0 Hz, 1H), 8.36 (s, 1H), 7.89-7.56 (m, 9H), 6.92 (dd, *J* = 10.0, 7.3 Hz, 1H), 5.95 (d, *J* = 7.3 Hz, 1H), 2.32 (s, 3H); EIMS (70 eV) *m/z*: 321 (M^++1, 24), 320 (M^+, 75), 133 (12), 105 (100), 91 (17), 77 (78). Anal. Calcd for $C_{18}H_{16}N_4O_2$: C, 67.50; H, 5.00; N, 17.50. Found: C, 67.47; H, 5.12; N, 17.45.

N-{2-[1-(4-Chlorophenyl)-5-oxo-1,5-dihydro-[1,2,4]triazol-4-yl]vinyl}oxalamic acid ethyl ester 7Cb

mp 146-147 °C; IR (KBr) 3100, 3064, 2986, 1761, 1713, 1683 cm^{-1}; ^1H NMR (DMSO-d_6) δ 11.23 (d, *J* = 10.2 Hz, 1H), 8.39 (s, 1H), 7.90 (d, *J* = 8.9 Hz, 2H), 7.56 (d, *J* = 8.9 Hz, 2H), 6.64 (dd, *J* = 10.2, 7.7 Hz, 1H), 6.06 (d, *J* = 7.7 Hz, 1H), 4.26 (q, *J* = 7.0 Hz, 2H), 1.25 (t, *J* = 7.0 Hz, 3H); EIMS (70 eV) *m/z*: 338 (M^++2, 10), 336 (M^+, 32), 263 (100), 153 (14), 125 (21), 111 (12), 75 (7). Anal. Calcd for $C_{14}H_{13}ClN_4O_4$: C, 50.00; H, 3.87; N, 16.67; Cl, 10.42. Found: C, 49.91; H, 3.90; N, 16.72; Cl, 10.34.

N-{2-[1-(4-Methylphenyl)-5-oxo-1,5-dihydro-[1,2,4]triazol-4-yl]vinyl}oxalamic acid ethyl ester 7Cc

mp 195-196 °C; IR (KBr) 3136, 3064, 2986, 1755, 1701, 1680 cm^{-1}; ^1H NMR (DMSO-d_6) δ 11.36 (d, *J* = 10.2 Hz, 1H), 8.35 (s, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.61 (dd, *J* = 10.2, 7.7 Hz, 1H), 6.08 (d, *J* = 7.7 Hz, 1H), 4.26 (q, *J* = 7.0 Hz, 2H), 2.32 (s, 3H), 1.27 (t, *J* = 7.0 Hz, 3H); EIMS (70 eV) *m/z*: 316 (M^+, 33), 243 (100), 133 (12), 105 (15), 91 (16), 55 (11). Anal. Calcd for $C_{15}H_{16}N_4O_4$: C, 56.96; H, 5.06; N, 17.72. Found: C, 56.76; H, 5.08; N, 17.71.

N-{2-[1-(4-Chlorophenyl)-5-oxo-1,5-dihydro-[1,2,4]triazol-4-yl]vinyl}acetamide 7Db

mp 181-182 °C; IR (KBr) 3184, 3106, 1719, 1680 cm^{-1}; ^1H NMR (DMSO-d_6) δ 9.88 (d, *J* = 10.6 Hz, 1H), 8.28 (s, 1H), 7.94 (d, *J* = 9.0 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 2H), 6.87 (dd, *J* = 10.6, 6.9 Hz, 1H), 5.65 (d, *J* = 6.9 Hz, 1H), 1.97 (s, 3H); EIMS (70 eV) *m/z*: 280 (M^++2, 38), 278 (M^+, 97), 236 (100), 153 (29), 125 (58), 111 (20), 85 (86), 75 (18), 69 (20), 63 (20), 56(38). Anal. Calcd for $C_{12}H_{11}ClN_4O_2$: C, 51.80; H, 3.96; N, 20.14; Cl, 12.59. Found: C, 51.75; H, 4.04; N, 20.22; Cl, 12.55.

N-{2-[1-(4-Methylphenyl)-5-oxo-1,5-dihydro-[1,2,4]triazol-4-yl]vinyl}acetamide 7Dc

mp 168-169 °C; IR (KBr) 3274, 3208, 3130, 3076, 3034, 1707, 1662 cm^{-1}; ^1H NMR (DMSO-d_6) δ 9.88 (d, *J* = 10.6 Hz, 1H), 8.23 (s, 1H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 6.83 (dd, *J* = 10.6, 6.9 Hz, 1H), 5.66 (d, *J* = 6.9 Hz, 1H), 2.31 (s, 3H) 1.97 (s, 3H); EIMS (70 eV) *m/z*: 259 (M^++1, 28), 258 (M^+, 100), 153 (22), 133 (29), 125 (60), 105 (12), 91 (32). Anal. Calcd for $C_{13}H_{14}N_4O_2$: C, 60.47; H, 5.43; N, 21.71. Found: C, 60.38; H, 5.47; N, 21.62.

2-(4-Chlorophenyl)-4-(ethyl-N-vinylcarbamate)-2,4-dihydro-[1,2,4]triazol-3-one 7Eb

mp 233-234 °C; IR (KBr) 3454, 3184, 3100, 2986, 1725, 1713, 1695 cm^{-1}; ^1H NMR (DMSO-d_6) δ 9.62 (d, *J* = 10.6 Hz, 1H), 8.19 (s, 1H), 7.91 (d, *J* = 8.9 Hz, 2H), 7.53 (d, *J* = 8.9 Hz, 2H), 6.65 (dd, *J* = 10.6, 6.8 Hz, 1H), 5.58 (d, *J* = 6.8 Hz, 1H), 4.09 (q, *J* = 7.0 Hz, 2H), 1.19 (t, *J* = 7.0 Hz, 3H); EIMS (70 eV) *m/z*: 310 (M^++2, 39), 308 (M^+, 100), 262 (39), 153 (37), 125 (62), 111 (28), 85 (59), 75 (17), 69 (30), 63 (19), 56 (27). Anal. Calcd for $C_{13}H_{13}ClN_4O_3$: C, 50.56; H, 4.22; N, 18.18; Cl, 11.36. Found: C, 50.45; H, 4.23; N, 18.13; Cl, 11.51.

2-(4-Methylphenyl)-4-(ethyl-N-vinylcarbamate)-2,4-dihydro-[1,2,4]triazol-3-one 7Ec

mp 164-165 °C; IR (KBr) 3304, 3088, 2980, 1722, 1710, 1698 cm^{-1}; ^1H NMR (DMSO-d_6) δ 9.60 (d, *J* = 10.2 Hz, 1H), 8.10 (s, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 6.61 (dd, *J* = 10.2, 7.3 Hz, 1H), 5.23 (d, *J* = 7.3 Hz, 1H), 3.94 (q, *J* = 7.0 Hz, 2H), 2.30 (s, 3H), 1.11 (t, *J* = 7.0 Hz, 3H); EIMS (70 eV) *m/z*: 288 (M^+, 6), 189 (100), 133 (8), 117 (9), 105 (6), 89 (6). Anal. Calcd for $C_{14}H_{16}N_4O_3$: C, 58.33; H, 5.59; N, 19.43. Found: C, 58.20; H, 5.45; N, 19.40.

The reaction of 3 with acyl chloride or acetic acid anhydride

3c (0.217 g, 1 mmol) dissolved in iPrOH (10 mL) was stirred with various acyl chlorides or acetic acid anhydride (2 mmol) at 70 °C for 2 hours. After the reaction, the precipitate was filtered and then recrystalized from EtOAc + iPrOH to obtain **8**.

5-(4-Nitrophenyl)-3-p-tolyl-3*H*-[1,3,4]oxadiazol-2-one 8Ac

mp 203-204 °C; IR (KBr) 3106, 3070, 3034, 2920, 1782 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.40 (d, *J* = 9.2 Hz, 2H), 8.14 (d, *J* = 9.2 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 2.34 (s, 3H); EIMS (70 eV) *m/z*: 297 (M^+, 30), 105 (100), 78 (13), 65 (5). Anal. Calcd for $C_{15}H_{11}N_3O_4$: C, 60.60; H, 3.70; N, 14.10. Found: C, 60.53; H, 3.76; N, 14.15.

5-Phenyl-3-p-tolyl-3*H*-[1,3,4]oxadiazol-2-one 8Bc

mp 165-166 °C; IR (KBr) 3133, 3084, 2920, 1776 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.90 (m, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.61 (m, 3H), 7.33 (d, *J* = 8.5 Hz, 2H), 2.34 (s, 3H); EIMS (70 eV) *m/z*: 252 (M^+, 56), 105 (100), 77 (13), 65 (5). Anal. Calcd for $C_{15}H_{12}N_2O_2$: C, 71.40; H, 4.80; N, 11.10. Found: C, 71.25;

H, 4.78; N, 11.15.

5-Oxo-4-p-tolyl-4,5-dihydro-[1,3,4]oxadiazol-2-carboxylic acid ethyl ester 8Cc

The spectrum of **8Cc** was the same as that reported in another paper.[7]

5-Methyl-3-p-tolyl-3*H*-[1,3,4]oxadiazol-2-one 8Dc

The spectrum of **8Dc** was the same as that reported in another paper.[1,6]

The reaction of 1 with acyl chloride or acetic acid anhydride

1c (0.217 g, 1 mmol) suspended in THF (5 mL) was stirred with various acyl chloride or acetic acid anhydride (2 mmol) at room temperature for 2 hours. After the reaction, THF was removed from the reaction mixture and then the residue was stirred with cold iPrOH for 30 minutes. The precipitate was filtered to obtain **8**.

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Key Words

α-Chloroformylarylhydrazine hydrochloride; Imidazole; 1,2,4-Triazole; α-Imidazolformylarylhydrazine; α-[1,2,4]Triazolformylarylhydrazine; 2,2′-Diaryl-2*H*,2′*H*-[4,4′]bi[[1,2,4]-triazolyl]-3,3′-dione; Cycloaddition; 2-Aryl-4-(2-aryl-4-vinyl-semicarbazide-4-yl)-2,4-dihydro-[1,2,4]-triazol-3-one; Acyl chloride; Acetic acid anhydride; 5-Substituted-3-aryl-3*H*-[1,3,4]oxadiazol-2-one.

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