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Received March 21, 1996

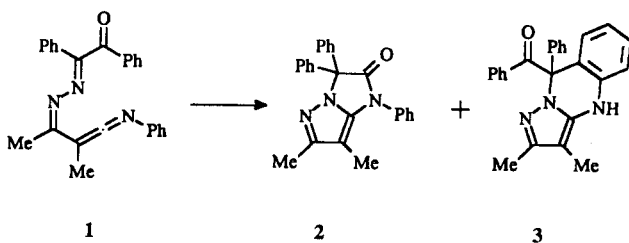
Revised July 16, 1996

The reaction of benzil 1-ureidoethylidene hydrazones **8** with a mixture of triphenylphosphine, carbon tetrachloride, and triethylamine provides a general route to 7*H*-imidazo[1,2-*b*][1,2,4]triazoles **18** via the thermal reaction of the expected keto azine carbodiimide intermediates **13**, and the structure of **18** was confirmed by X-ray crystallographic analysis.

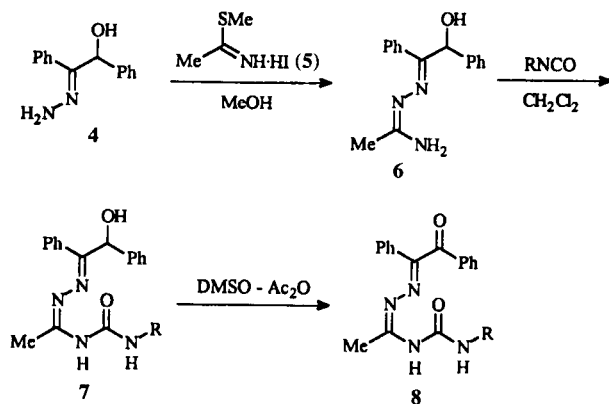
*J. Heterocyclic Chem.*, **34**, 71 (1997).

The electrocyclic reaction of conjugated heterocumulenes as a synthetic route to heterocycles [1], prompts us to report on our studies and we recently described a new route to 1,2,4-triazole fused heterocycles such as 5,10-dihydro-1,2,4-triazolo[5,1-*b*]quinazolines [2], 4*H*-1,2,4-triazolo[1,5-*c*][1,3,5]oxadiazines [3], 5,6-dihydro-7*H*-imidazo[1,2-*b*][1,2,4]triazoles [4], and 5,6-dihydro-1,2,4-triazolo[5,1-*d*][1,3,5]oxadiazepines [4] involving electrocyclic cyclization of azino carbodiimides or *N*-aziridinylimino carbodiimides obtained from the corresponding ureas as using Appel's dehydration method [5].

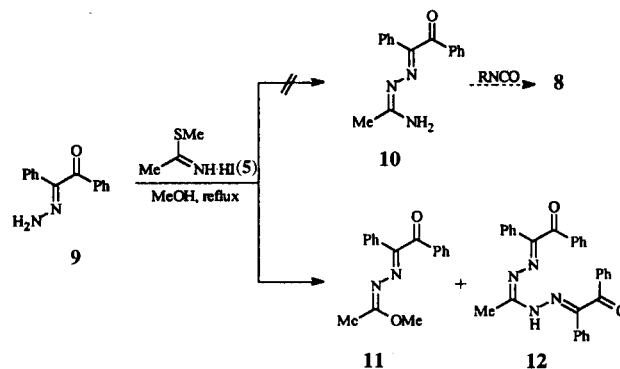
Scheme I



Scheme II



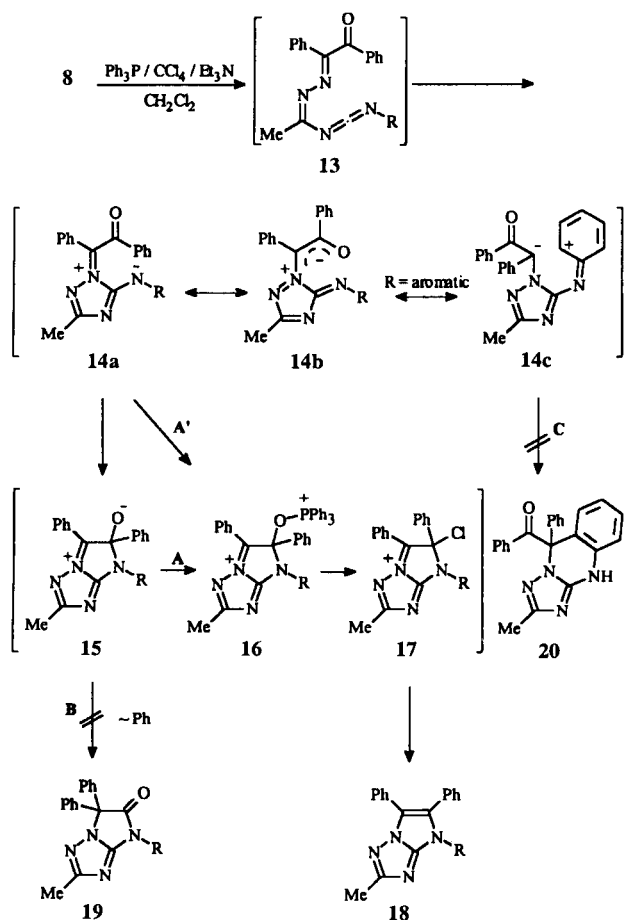
Scheme III



Also, Schweizer and co-workers reported on a synthesis of 2,3-dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-ones **2** and 4,9-dihydropyrazolo[5,1-*b*]quinazolines **3** based on the thermal rearrangement of keto azine ketimines **1** [6] (Scheme I). The present study was undertaken to examine a thermal reaction of keto azine carbodiimides **13** to prepare 5,6-dihydro-7*H*-imidazo[1,2-*b*][1,2,4]triazol-6-ones **19**, and the unexpected 7*H*-imidazo[1,2-*b*][1,2,4]triazoles **18** obtained during the course of this investigation is the subject of this publication (Scheme IV). The methods hitherto reported for the preparation of imidazo[1,2-*b*][1,2,4]triazoles either use imidazole derivatives as starting materials [7-10] or start from derivatives of the 1,2,4-triazole ring [11-15].

The starting compounds, benzil 1-ureidoethylidene hydrazones **8** employed in this study, were prepared from benzoin hydrazone **4** in three steps as depicted in Scheme II. Benzoin hydrazone **4** was treated with *S*-methylthioacetimidate hydroiodide **5** [16] in refluxing methanol followed by neutralization with aqueous sodium hydrogen carbonate to give benzoin 1-aminoethylidene hydrazone **6** in 95% yield. Compound **6** was reacted with an equivalent

Scheme IV



of isocyanates in dichloromethane at room temperature to give benzoin 1-ureidoethylidene hydrazones **7** in 92-97% yields (Table 1). Compound **7** was subsequently oxidized by dimethyl sulfoxide-acetic anhydride [17] at room temperature to afford desired benzil 1-ureidoethylidene hydrazone **8** in 66-77% yields (Table 2). Unfortunately, the

preparation of benzil 1-aminoethylidene hydrazone **10** as the first choice of starting material by the reaction of benzil monohydrazone **9** with *S*-methylthioacetimidate hydroiodide **5** was unsuccessful due to the formation of unusual benzil 1-methoxyethylidene hydrazone **11** and benzil bishydrazone **12** (Scheme III).

When benzil 1-ureidoethylidene hydrazones **8** were treated with three equivalents of triphenylphosphine, carbon tetrachloride, and triethylamine in refluxing dichloromethane, the only product obtained was the 7*H*-imidazo[1,2-*b*][1,2,4]triazoles **18** in 65-87% yields (Table 3), neither 5,6-dihydro-7*H*-imidazo[1,2-*b*][1,2,4]triazol-6-ones **19** nor 1,2,4-triazolo[5,1-*b*]quinazolines **20** as previously reported in the similar system [6]. A plausible mechanism for the transformation of **8** into **18** is shown in Scheme IV. Nucleophilic attack by the imine nitrogen on the carbodiimide carbon in intermediate **13** would give

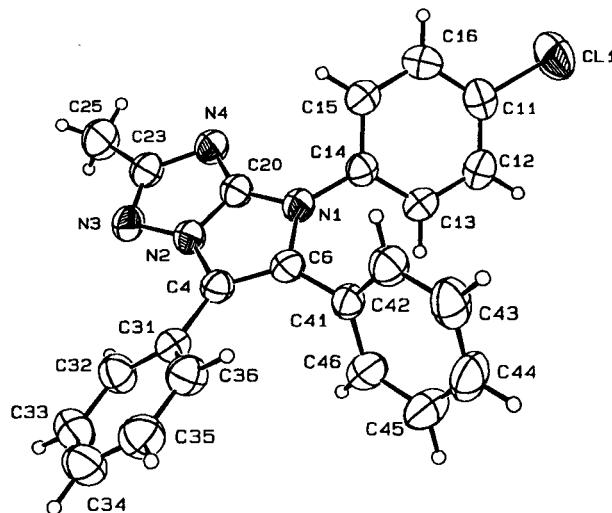
Figure. An ORTEP Diagram of **18b**.

Table 1  
Benzoin 1-Ureidoethylidene Hydrazones **7** Prepared

	R	Yield (%)	Mp (°C)	Molecular Formula	Analysis %		
					C	H	N
<b>7a</b>	C <sub>6</sub> H <sub>5</sub>	96	193-195	C <sub>23</sub> H <sub>22</sub> N <sub>4</sub> O <sub>2</sub>	71.48	5.74	14.40
					71.24	5.86	14.49
<b>7b</b>	4-ClC <sub>6</sub> H <sub>4</sub>	97	191-192	C <sub>23</sub> H <sub>21</sub> ClN <sub>4</sub> O <sub>2</sub>	65.63	5.03	13.31
					65.48	5.08	13.29
					68.31	5.23	13.85
<b>7c</b>	2-FC <sub>6</sub> H <sub>4</sub>	92	176-177	C <sub>23</sub> H <sub>21</sub> FN <sub>4</sub> O <sub>2</sub>	68.11	5.27	13.81
					69.22	5.81	13.45
<b>7d</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	95	185-186	C <sub>24</sub> H <sub>24</sub> N <sub>4</sub> O <sub>3</sub>	69.18	5.89	13.46
					66.65	6.21	17.27
<b>7e</b>	CH <sub>3</sub> [a]	95	202-203	C <sub>18</sub> H <sub>20</sub> N <sub>4</sub> O <sub>2</sub>	66.62	6.38	17.26

[a] The reaction was refluxed.

Table 2

Benzil 1-Ureidoethylidene Hydrazones **8** Prepared

	R	Yield (%)	Mp (°C)	Molecular Formula	Analysis %		
					Calcd./Found	C	H
<b>8a</b>	C <sub>6</sub> H <sub>5</sub>	67	175-176	C <sub>23</sub> H <sub>20</sub> N <sub>4</sub> O <sub>2</sub>	71.86	5.24	14.57
					71.59	5.40	14.28
<b>8b</b>	4-ClC <sub>6</sub> H <sub>4</sub>	77	186-187	C <sub>23</sub> H <sub>19</sub> ClN <sub>4</sub> O <sub>2</sub>	65.95	4.57	13.38
					65.66	4.41	13.15
<b>8c</b>	2-FC <sub>6</sub> H <sub>4</sub>	69	189-190	C <sub>23</sub> H <sub>19</sub> FN <sub>4</sub> O <sub>2</sub>	68.64	4.76	13.92
					68.78	4.76	13.70
<b>8d</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	67	181-182	C <sub>24</sub> H <sub>22</sub> N <sub>4</sub> O <sub>3</sub>	69.55	5.35	13.52
					69.37	5.31	13.48
<b>8e</b>	CH <sub>3</sub>	66	176-177	C <sub>18</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub>	67.07	5.63	17.38
					66.89	5.45	17.08

Table 3

5,6-Diphenyl-2-methyl-7*H*-imidazo[1,2-*b*][1,2,4]triazoles **18** Prepared

	R	Yield (%)	Mp (°C)	Molecular Formula	Mass Spectrum m/z (%)	Analysis %		
						Calcd./Found	C	H
<b>18a</b>	C <sub>6</sub> H <sub>5</sub>	86	257-258	C <sub>23</sub> H <sub>18</sub> N <sub>4</sub>	350 (M <sup>+</sup> , 37), 180	78.83	5.18	15.99
					(100), 103 (9), 77 (43)	78.64	5.09	15.72
<b>18b</b>	4-ClC <sub>6</sub> H <sub>4</sub>	86	216-217	C <sub>23</sub> H <sub>17</sub> ClN <sub>4</sub>	386 (18), 384 (M <sup>+</sup> , 52)	71.78	4.45	14.56
					214 (100), 216 (34),	71.91	4.24	14.31
					111 (17)			
<b>18c</b>	2-FC <sub>6</sub> H <sub>4</sub>	87	192-193	C <sub>23</sub> H <sub>17</sub> FN <sub>4</sub>	368 (M <sup>+</sup> , 42), 198	74.99	4.65	15.21
					(100), 95 (7), 77 (13)	74.67	4.67	15.21
<b>18d</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	84	195-196	C <sub>24</sub> H <sub>20</sub> N <sub>4</sub> O	380 (M <sup>+</sup> , 59), 210	75.77	5.30	14.73
					(100), 92 (7), 77 (14)	75.51	5.11	14.68
<b>18e</b>	CH <sub>3</sub>	65	144-145	C <sub>18</sub> H <sub>16</sub> N <sub>4</sub>	288 (M <sup>+</sup> , 54), 118	74.98	5.59	19.43
					(100), 77 (18)	74.78	5.42	19.31

Table 4

<sup>1</sup>H-NMR Data of Compounds **7** [a], **8** [a] and **18** [b]

<b>7a</b>	2.34 (s, 3H), 5.66 (d, 1H, J = 3.6 Hz), 6.00 (d, 1H, J = 3.7 Hz), 6.53-6.55 (m, 2H), 6.91-7.30 (m, 13H), 9.58 (s, 1H), 11.07 (s, 1H)
<b>7b</b>	2.31 (s, 3H), 5.63 (d, 1H, J = 3.9 Hz), 5.99 (d, 1H, J = 4.1 Hz), 6.48-6.51 (m, 2H), 7.04-7.30 (m, 12H), 9.63 (s, 1H), 11.18 (s, 1H)
<b>7c</b>	2.26 (s, 3H), 5.66 (d, 1H, J = 4.3 Hz), 5.98 (d, 1H, J = 4.4 Hz), 6.97-7.29 (m, 14H), 9.60 (s, 1H), 10.71 (s, 1H)
<b>7d</b>	2.30 (s, 3H), 3.66 (s, 3H), 5.63 (d, 1H, J = 4.2 Hz), 5.96 (d, 1H, J = 4.2 Hz), 6.47 (d, 2H, J = 8.9 Hz), 6.65 (d, 2H, J = 8.9 Hz), 7.03-7.28 (m, 10H), 9.47 (s, 1H), 10.85 (s, 1H)
<b>7e</b>	2.20 (s, 6H), 5.62 (d, 1H, J = 4.3 Hz), 5.95 (d, 1H, J = 4.4 Hz), 6.93-7.29 (m, 10H), 8.43 (br s, 1H), 9.13 (s, 1H)
<b>8a</b>	2.23 (s, 3H), 6.62-6.64 (m, 2H), 6.97-7.68 (m, 11H), 8.03-8.05 (m, 2H), 10.02 (s, 1H), 11.12 (s, 1H)
<b>8b</b>	2.23 (s, 3H), 6.61-6.63 (m, 2H), 7.17-7.68 (m, 10H), 8.03-8.05 (m, 2H), 10.10 (s, 1H), 11.24 (s, 1H)
<b>8c</b>	2.23 (s, 3H), 7.09-7.79 (m, 12H), 8.01-8.04 (m, 2H), 10.07 (s, 1H), 10.81 (s, 1H)
<b>8d</b>	2.23 (s, 3H), 3.70 (s, 3H), 6.60 (d, 2H, J = 7.8 Hz), 6.72 (d, 2H, J = 7.6 Hz), 7.36-7.68 (m, 8H), 8.04-8.06 (m, 2H), 9.97 (s, 1H), 10.94 (s, 1H)
<b>8e</b>	2.15 (s, 3H), 2.39 (d, 3H, J = 3.9 Hz), 7.42-7.69 (m, 8H), 8.01-8.03 (m, 2H), 8.64 (s, 1H), 9.69 (br s, 1H)
<b>18a</b>	2.55 (s, 3H), 7.27-7.32 (m, 13H), 7.65-7.68 (m, 2H)
<b>18b</b>	2.55 (s, 3H), 7.18-7.37 (m, 12H), 7.63-7.66 (m, 2H)
<b>18c</b>	2.55 (s, 3H), 7.11-7.36 (m, 12H), 7.69-7.71 (m, 2H)
<b>18d</b>	2.53 (s, 3H), 3.74 (s, 3H), 6.81 (d, 2H, J = 8.6 Hz), 7.16 (d, 2H, J = 8.6 Hz), 7.24-7.30 (m, 8H), 7.65-7.67 (m, 2H)
<b>18e</b>	2.54 (s, 3H), 3.51 (s, 3H), 7.18-7.61 (m, 10H)

[a] Dimethyl-d<sub>6</sub> sulfoxide. [b] Deuteriochloroform.

the resonance-stabilized azomethine imine **14a-14c**. In **14a**, the exocyclic anionic nitrogen would attack the carbonyl group and resulting oxy anion **15** react with chlo-

rotriphenylphosphonium ion, or would attack directly the chlorotriphenylphosphonium ion chelated carbonyl group, to give alkoxyphosphonium ion **16**, which is converted to

Table 5

Crystal and Refinement Data for **18b**

formula	C <sub>23</sub> H <sub>17</sub> ClN <sub>4</sub>
formula weight	384.86
crystal system	monoclinic
space group	P2 <sub>1</sub> /c
a, Å	10.611 (4)
b, Å	8.392 (3)
c, Å	22.067 (5)
β, deg	92.05 (3)
V, Å <sup>3</sup>	1964 (1)
Z	4
F (000)	800
density (calc.), g/cm <sup>3</sup>	1.302
crystal size, mm	0.24 x 0.21 x 0.30
μ, absorption coef., mm <sup>-1</sup>	0.210
2Theta (max), deg.	50.20
index ranges	-12 ≤ h ≤ 12, 0 ≤ k ≤ 9, 0 ≤ l ≤ 26
reflections collected	2823
independent reflections	2704
parameters refined	253
GOF [a]	1.050
final R indices [I > 2 σ (I)]	R1 = 0.0460, wR2 = 0.1209 [b]
R indices (all data)	R1 = 0.0473, wR2 = 0.1225
largest diff. peak and hole, e · Å <sup>-3</sup>	0.285 and -0.232

[a] GOF = [Σ (w(F<sub>o</sub> - F<sub>c</sub>)<sup>2</sup>) / (No. of reflections - No. of parameters)]<sup>1/2</sup>;  
 [b] R1 = Σ ||F<sub>o</sub> - F<sub>c</sub>|| / Σ |F<sub>o</sub>|, wR2 = {Σw (F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)<sup>2</sup> / ΣwF<sub>o</sub><sup>4</sup>}<sup>1/2</sup>,  
 where w = 1 / [σ<sup>2</sup>F<sub>o</sub><sup>2</sup> + (0.0754P)<sup>2</sup> + 0.55P], P = {Max (F<sub>o</sub><sup>2</sup>, 0) + 2F<sub>o</sub><sup>2</sup>}/3.

the chloride **17** by loss of triphenylphosphine oxide and subsequent elimination of chlorine by triphenylphosphine would give compound **18**.

In an attempt to block the reaction between resulting oxy anion or the carbonyl group and chlorotriphenylphosphonium ion, on the assumption that competition reaction between pathway A, A', B and C might be occurred and that possibly compounds **19** or **20** would be formed, one equivalent of triphenylphosphine was used in the reaction of **8a**. However, neither compound **19** nor **20** were obtained, and 27% yield of **18a**, and 42% yield of recovered unchanged urea **8a** were obtained.

The structure elucidation of **18** was based on X-ray crystallographic analysis. An ORTEP diagram of **18b** is shown in the Figure. Crystal and refinement data, atomic coordinates, bond lengths, and bond angles are provided in Tables 5, 6 and 7, respectively. The structure presents no marked deviations from typical bond lengths and bond angles.

We have thus worked out a useful method for the synthesis of 7*H*-imidazo[1,2-*b*][1,2,4]triazoles **18** from keto azine ureas **8** using Appel's dehydration condition.

Table 6

Atomic Coordinates (x 10<sup>4</sup>) and Equivalent Isotropic Displacement Parameters (Å<sup>2</sup> x 10<sup>3</sup>) for **18b**

	X	Y	Z	U(eq)
Cl(1)	898(1)	2128(1)	3114(1)	92(1)
N(1)	4618(2)	2490(2)	5187(1)	45(1)
N(2)	6440(2)	2680(2)	5684(1)	44(1)
N(3)	7730(2)	2643(2)	5651(1)	49(1)
N(4)	6726(2)	2299(2)	4712(1)	52(1)
C(4)	5538(2)	2821(2)	6123(1)	43(1)
C(6)	4406(2)	2718(2)	5805(1)	43(1)
C(11)	1992(2)	2229(3)	3725(1)	54(1)
C(12)	1861(2)	3391(3)	4157(1)	53(1)
C(13)	2722(2)	3482(2)	4640(1)	47(1)
C(14)	3716(2)	2408(2)	4688(1)	42(1)
C(15)	3858(2)	1268(3)	4241(1)	51(1)
C(16)	2994(2)	1169(3)	3758(1)	58(1)
C(20)	5896(2)	2467(2)	5135(1)	45(1)
C(23)	7827(2)	2420(3)	5063(1)	51(1)
C(25)	9086(2)	2355(4)	4787(1)	75(1)
C(31)	5878(2)	2958(2)	6774(1)	45(1)
C(32)	6967(2)	3738(3)	6980(1)	56(1)
C(33)	7279(2)	3845(3)	7593(1)	67(1)
C(34)	6509(3)	3185(3)	8010(1)	67(1)
C(35)	5435(3)	2400(3)	7810(1)	63(1)
C(36)	5114(2)	2276(3)	7201(1)	54(1)
C(41)	3121(2)	2816(2)	6032(1)	44(1)
C(42)	2288(2)	1546(3)	5963(1)	54(1)
C(43)	1095(2)	1668(4)	6188(1)	68(1)
C(44)	740(2)	3027(4)	6477(1)	75(1)
C(45)	1557(2)	4288(4)	6546(1)	77(1)
C(46)	2748(2)	4186(3)	6323(1)	61(1)

\* Equivalent isotropic U defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor.

## EXPERIMENTAL

All reagents and solvents were reagent grade or were purified by standard methods before use and the reactions were routinely carried out under an inert atmosphere. Silica gel 60 (70-230 mesh ASTM) used for column chromatography was supplied by E. Merck. Analytical thin layer chromatography (tlc) was performed on silica gel with fluorescent indicator coated on aluminium sheets. Melting points were taken using an Electrothermal melting point apparatus and are uncorrected. Microanalyses were obtained using a Carlo Erba EA 1180 element analyzer. The mass spectra were recorded on a Hewlett Packard model 5972 spectrometer with an electron beam energy of 70 eV. Infrared spectra were recorded on a Nicolet Magna 550 FTIR spectrometer. The <sup>1</sup>H and <sup>13</sup>C nmr spectra were measured on a Gemini 300 spectrometer. All chemical shifts are reported in parts per million (δ) relative to tetramethylsilane. X-ray structure determination was confirmed using an Enraf-Nonius CAD-4 automatic diffractometer.

The *S*-methylthioacetimidate hydroiodide [16] and benzoin hydrazone [18] were prepared following the literature procedures. Benzoin, benzil monohydrazone, and isocyanates were purchased from Aldrich Chemical Company.

Table 7

Bond Lengths (Å) and Bond Angles (deg) for **18b**

Cl (1)-C (11)	1.750 (2)	C (13)-C (14)	1.389 (3)
N (1)-C (20)	1.365 (3)	C (14)-C (15)	1.385 (3)
N (1)-C (6)	1.403 (3)	C (15)-C (16)	1.383 (3)
N (1)-C (14)	1.434 (3)	C (23)-C (25)	1.489 (3)
N (2)-C (20)	1.335 (2)	C (31)-C (36)	1.387 (3)
N (2)-N (3)	1.374 (2)	C (31)-C (32)	1.390 (3)
N (2)-C (4)	1.391 (3)	C (32)-C (33)	1.383 (3)
N (3)-C (23)	1.318 (3)	C (33)-C (34)	1.370 (4)
N (4)-C (20)	1.314 (3)	C (34)-C (35)	1.375 (4)
N (4)-C (23)	1.382 (3)	C (35)-C (36)	1.379 (3)
N (4)-C (6)	1.373 (3)	C (41)-C (46)	1.381 (3)
C (4)-C (31)	1.473 (3)	C (41)-C (42)	1.390 (3)
C (6)-C (41)	1.472 (3)	C (42)-C (43)	1.379 (3)
C (11)-C (12)	1.375 (3)	C (43)-C (44)	1.367 (4)
C (11)-C (16)	1.386 (3)	C (44)-C (45)	1.373 (4)
C (12)-C (13)	1.379 (3)	C (45)-C (46)	1.375 (3)
C (20)-N (1)-C (6)	106.1 (2)	C (11)-C (16)-C (15)	119.3 (2)
C (20)-N (1)-C (14)	124.9 (2)	N (4)-C (20)-N (2)	112.3 (2)
C (6)-N (1)-C (14)	128.9 (2)	N (4)-C (20)-N (1)	138.9 (2)
C (20)-N (2)-N (3)	110.4 (2)	N (2)-C (20)-N (1)	108.8 (2)
C (20)-N (2)-C (4)	110.9 (2)	N93)-C (23)-N (4)	117.9 (2)
N (3)-N (2)-C (4)	138.7 (2)	N (3)-C (23)-C (25)	120.7 (2)
C (23)-N (3)-N (2)	99.7 (2)	N (4)-C (23)-C (25)	121.4 (2)
C (20)-N (4)-C (23)	99.7 (2)	C (36)-C (31)-C (32)	118.2 (2)
C (6)-C (4)-N (2)	104.4 (2)	C (36)-C (31)-C (4)	120.1 (2)
C (6)-C (4)-C (31)	133.1 (2)	C (32)-C (31)-C (4)	121.7 (2)
N (2)-C (4)-C (31)	122.4 (2)	C (33)-C (32)-C (31)	121.1 (2)
C (4)-C (6)-N (1)	109.8 (2)	C (34)-C (33)-C (32)	120.2 (2)
C (4)-C (6)-C (41)	128.8 (2)	C (33)-C (34)-C (35)	119.1 (2)
N (1)-C (6)-C (41)	121.5 (2)	C (34)-C (35)-C (36)	121.4 (2)
C (12)-C (11)-C (16)	120.9 (2)	C (35)-C (36)-C (31)	120.0 (2)
C (12)-C (11)-Cl (1)	119.2 (2)	C (46)-C (41)-C (42)	119.8 (2)
C (16)-C (11)-Cl (1)	119.8 (2)	C (46)-C (41)-C (6)	119.3 (2)
C (11)-C (12)-C (13)	119.6 (2)	C (42)-C (41)-C (6)	120.8 (2)
C (12)-C (13)-C (14)	120.2 (2)	C (43)-C (42)-C (41)	119.5 (2)
C (15)-C (14)-C (13)	119.7 (2)	C (44)-C (43)-C (42)	120.1 (2)
C (15)-C (14)-N (1)	119.5 (2)	C (43)-C (44)-C (45)	120.7 (2)
C (13)-C (14)-N (1)	120.8 (2)	C (44)-C (45)-C (46)	119.8 (3)
C (14)-C (15)-C (16)	120.2 (2)	C (45)-C (46)-C (41)	120.0 (2)

\* Symmetry transformations used to generate equivalent atoms.

**Benzoin 1-Aminoethylidene Hydrazone 6.**

To a solution of benzoin hydrazone (**4**, 4.53 g, 20 mmoles) in 100 ml of methanol was added *S*-methylthioacetimidate hydroiodide (**5**, 5.64 g, 26 mmoles) and this solution was stirred at reflux temperature for 0.5 hour. After cooling to room temperature the solvent was removed on a rotavapor and the residue was partitioned between aqueous sodium hydrogen carbonate solution and dichloromethane. The dichloromethane layer was washed with water and the solvent was removed after drying over magnesium sulfate, and the residue was crystallized with petroleum ether to give 5.08 g (95%) of **6**, mp 106–107°; <sup>1</sup>H nmr (deuteriochloroform): δ 1.96 (s, 3H), 5.12 (br s, 3H), 5.63 (s, 1H), 7.16–7.27 (m, 10H); <sup>13</sup>C nmr (deuteriochloroform): δ 161.2, 158.3, 140.9, 134.2, 128.9, 128.8, 128.4, 128.1, 127.8, 127.5, 75.9, 19.8; ir (potassium bromide): 3409, 3333, 3241,

1632, 1576, 1495, 1403, 1291, 1260, 1194, 1097, 1021, 705, 624 cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>16</sub>H<sub>17</sub>N<sub>3</sub>O: C, 71.89; H, 6.41; N, 15.79. Found: C, 71.78; H, 6.46; N, 15.50.

**Benzoin 1-Ureidoethylidene Hydrazones 7. General Procedure.**

To a stirred solution of benzoin 1-aminoethylidene hydrazone (**6**, 1.34 g, 5 mmoles) in 25 ml of dichloromethane was added isocyanate (5 mmoles) at room temperature. The white solid was precipitated as soon as addition was completed. After stirring for 0.5 hour at ambient temperature, the precipitated solid was separated by filtration, washed with ether to give **7** (Table 1).

**Benzil 1-Ureidoethylidene Hydrazones 8. General Procedure.**

To a stirred solution of **7** (4 mmoles) in 20 ml of dry dimethyl sulfoxide was added 6 ml of acetic anhydride. The solution was stirred for 6 hours at room temperature and poured onto 100 g of ice. The mixture was made basic with saturated sodium hydrogen carbonate, and the resulting precipitate was filtered and washed with water, followed by recrystallization from ethanol to give **8** as a pale yellow solid (Table 2).

**Benzil 1-Methoxyethylidene Hydrazone 11 and Benzil Bis-hydrazone 12.**

To a suspension of benzil monohydrazone (**9**, 0.90 g, 4 mmoles) in 20 ml of methanol was added *S*-methylthioacetimidate hydroiodide (**5**, 0.87 g, 4 mmoles) and this mixture was stirred at reflux temperature for 1 hour. After cooling to room temperature the solvent was removed on a rotavapor and the residue was partitioned between aqueous sodium hydrogen carbonate solution and dichloromethane. The dichloromethane layer was washed with water and the solvent was removed after drying over magnesium sulfate, and the residue was chromatographed on silica gel column and eluted with hexane-ethyl acetate 3:1 to give 0.31 g (28%) [**19**] of **11** and 0.44 g (23%) [**19**] of **12** in the order of elution.

Compound **11** had mp 92–94° (dichloromethane-hexane); <sup>1</sup>H nmr (deuteriochloroform): δ 2.22 (s, 3H), 3.34 (s, 3H), 7.36–7.91 (m, 10H); <sup>13</sup>C nmr (deuteriochloroform): δ 198.5, 169.7, 162.3, 135.6, 133.4, 130.8, 130.4, 128.9, 128.7, 128.6, 127.1, 53.8, 14.5; ir (potassium bromide): 1678, 1625, 1569, 1496, 1453, 1374, 1293, 1229, 1052, 913, 689, 587 cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: C, 72.84; H, 5.75; N, 9.99. Found: C, 73.13; H, 5.60; N, 10.12.

Compound **12** had mp 184–185° (ethyl acetate); <sup>1</sup>H nmr (deuteriochloroform): δ 2.11 (s, 3H), 7.26–8.06 (m, 20H), 10.47 (s, 1H); <sup>13</sup>C nmr (deuteriochloroform): δ 198.2, 191.5, 161.2, 157.8, 146.8, 137.3, 135.3, 134.0, 132.9, 132.3, 130.9, 130.5, 130.0, 129.3, 129.1, 128.9, 128.8, 128.6, 128.3, 127.9, 127.1, 17.2; ir (potassium bromide): 3414, 3297, 1683, 1652, 1617, 1561, 1494, 1429, 1301, 1225, 1164, 1087, 1026, 945, 899, 695 cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>30</sub>H<sub>24</sub>N<sub>4</sub>O<sub>2</sub>: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.18; H, 5.11; N, 11.80.

**5,6-Diphenyl-2-methyl-7*H*-imidazo[1,2-*b*][1,2,4]triazoles 18. General Procedure.**

To a stirred solution of the appropriate urea **8** (3 mmoles) in 25 ml of dichloromethane was added triphenylphosphine (1.18 g, 4.5 mmoles), carbon tetrachloride (1.16 ml, 12 mmoles), and triethylamine (0.63 ml, 4.5 mmoles) and the mixture was heated

to reflux temperature. After 1 hour, the same amount of triphenylphosphine, carbon tetrachloride, and triethylamine was added once more, and the mixture was refluxed for 1 hour further. After cooling to room temperature the reaction mixture was partitioned between water and dichloromethane (15 ml x 2), and combine each other, and the solvent was removed after drying over magnesium sulfate. The residue was chromatographed on silica gel column and eluted with hexane-ethyl acetate 3:1 to yield the product **18** as a white solid (Table 3).

#### Crystallographic Structure Determination of **18b**.

A colorless crystal of  $C_{23}H_{17}ClN_4$ , **18b**, grown by slow evaporation of an ethanolic solution, belonged to the monoclinic space group  $P2_1/c$ :  $a = 10.611$  (4),  $b = 8.392$  (3),  $c = 22.067$  (5) Å,  $\beta = 92.05$  (3)°,  $V = 1964$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D$  (calcd.) = 1.302 gcm<sup>-3</sup>, and,  $\mu = 0.210$  mm<sup>-1</sup>. Of 2823 reflections collected at 23° ( $M_oK_{\alpha}$   $3.7^\circ \leq 2\theta \leq 50.20^\circ$ ), 2704 were unique with  $I > 2\sigma(I)$  were used in the solution and refinement of the structure. All non-hydrogen atoms were located by direct methods and subsequent difference Fourier syntheses. All hydrogen atoms were added at calculated positions. Refinement of all non-hydrogen atoms with anisotropic temperature factors (hydrogen atoms isotropic) led to convergence at  $R1 = 0.0460$ ,  $wR2 = 0.1209$ ,  $GOF = 1.050$ , with the highest peak on the final difference map of  $0.285$  e Å<sup>-3</sup>.

#### Acknowledgement.

We gratefully acknowledge the Korea Science and Engineering Foundation (Grant No. 941-0300-008-2) for support of this research.

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