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Reactions of benzils and urea in ethylene glycol at 180° for 1-2 hours gave 2,4,5-triaryloxazoles as major products and bicyclic imidazoimidazole-2,5-diones as minor products. *N*-Methylurea and *N*-phenylurea gave the oxazoles under similar conditions. The solvent seemed to assist the formation of oxazole by eliminating the isocyanate components as ethylene glycol biscarbamates.

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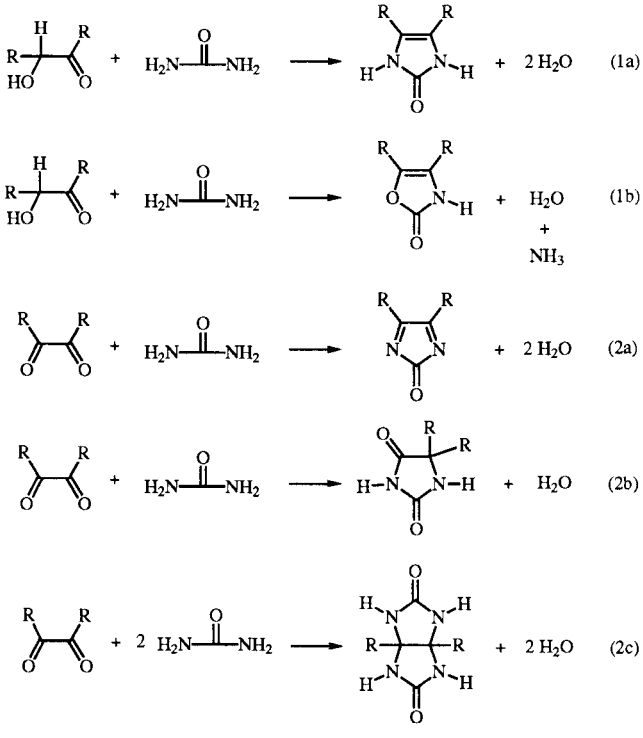
Reactions of α-hydroxyketones (acyloins) and α-diketones with ureas are widely known [1]. A stoichiometric chemical equation indicates that condensation of one mole of acyloin with one mole of urea will produce one mole of 4-imidazolin-2-one and two moles of water (Equation 1a). Alternatively, oxazolidin-2-one may be formed if water and ammonia are eliminated (Equation 1b). Many experimental results indicate that the former is the major pathway although there are exceptions depending on the reaction conditions [2,3].



Similar stoichiometric analogy (Equation 2a) would predict the formation of one mole of 2-imidazolone and two moles of water from one mole of α-diketone and one mole of urea. Alternatively, elimination of one mole of water and rearrangement of an R group would give a hydantoin derivative (Equation 2b). On the other hand, one mole of α-diketone may react with two moles of urea to form one mole of a bicyclic compound and two moles of water (Equation 2c). To our knowledge, however, there is no example of reaction illustrated in Equation 2a. Instead, the products are either oxazoles (*cf.* **3**) or bicyclic compounds (*cf.* **4**), or both, depending on the structural features of the diketones or reaction conditions. Other side products are also present such as imidazoles (*cf.* **5**) and benzoic acid derivatives (*cf.* **6**). For example, when a mixture of benzil (**1a**) and 10-fold excess of urea (**2a**) was heated at 220° for 15 minutes, a bicyclic compound **4a** was isolated in 50% yield in addition to 2,4,5-triphenylimidazole (**5a**, 3%) and 2,4,5-triphenyloxazole (**3a**, 28%) [4]. However, there are several examples which follow Equation 2c. For example, compound **4a** was also prepared by refluxing in trifluoroacetic acid and benzene for 6 hours or by refluxing in ethanol in the presence of hydrogen chloride, although no yield was reported [5]. An α-diketone having methyl and phenyl groups also gave a bicyclic-type of compound under similar conditions [6]. The reaction shown in Equation 2b is usually base catalyzed [7-10].

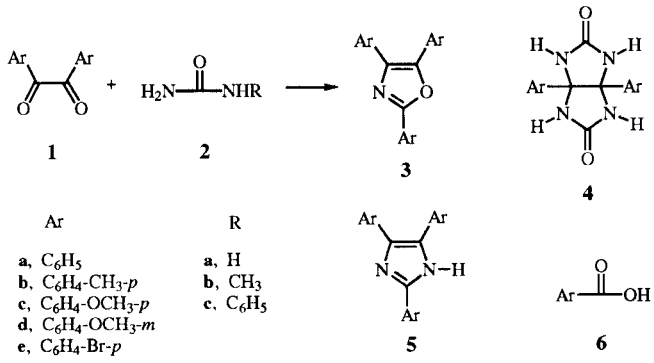
As we are interested in preparing 4,5-diarylimidazolones described in Equation 2 we reexamined the reactions of benzils and ureas under various conditions.

Results and Discussion.

When a neat mixture of **1a** and **2a** (1:3.5 by mole) was heated at 180° for 1 hour, **4a** was formed in 67% yield. The oxazole compound **3a** was isolated in less than 3% yield. Apparently, it was not necessary to use 10-fold excess of urea. Considering the required ratio of **1a** and **2a** is 1:2 in order to form **4a** the present conditions seem to be better than the one in the literature [4] because less than two-fold excess of urea is used and the reaction temperature is lower. When a mixture of **1a** and **2a** in similar ratio was heated in ethylene glycol at 180° for 1 hour the major product was **3a** (75%), and **4a** was isolated in 11% yield. On the other hand, refluxing a mixture of **1a** and **2a** in similar molar ratio in glacial acetic acid for 1 hour produced **3a** (34%), **4a** (41%), and **6a** (43%). We repeated the procedure reported by Butler, *et al* [5]. A mixture of **1a** and **2a** was refluxed in benzene in the presence of trifluoroacetic acid for 6 hours. This procedure afforded **4a**

in over 95% yield. When glacial acetic acid was employed instead of trifluoroacetic acid, less than 5% of **4a** was obtained and most of the starting materials were recovered after 9 hours of reflux. The yield of **4a** was again very high (>90%) when a mixture of **1a**, **2a**, and trifluoroacetic acid in toluene was heated at reflux for 6 hours, but some of **3a** and **6a** were present in the reaction mixture.

Scheme 1



Our results, which are summarized in Table 1, seem to suggest that there are two competing pathways in the reaction of benzil and urea. Formation of **4a** seems to be favorable in the presence of a strong acid catalyst (*eg.* trifluoroacetic acid or hydrochloric acid) at low temperature (bp of benzene). Acetic acid does not seem to be an effective catalyst when the reaction is carried out in benzene. On the other hand, formation of **3a** seems to be effective at high temperature (180°), especially, in the presence of a protic solvent.

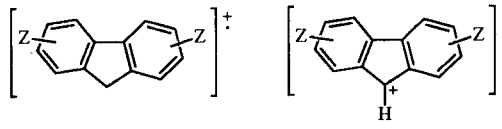
Table 1

Yields of **3** and **4** under Various Conditions

Benzils	Ethylene glycol	Direct heating	Reflux in acetic acid
1a	**3a** (75), **4a** (11)	**3a** (3), **4a** (67)	**3a** (48), **4a** (41)
1b	**3b** (67), **4b** (14)		
1c	**3c** (78), **4c** (0)	**3c** (8), **4c** (63)	**3c** (31), **4c**(15)
1d	**3d** (50), **4d** (37)		
1e	**3e** (50), **4e** (0)		

Other benzils having *m*- or *p*-substituents (**1b-e**) also gave both **3** and **4**, except *p,p*-dibromobenzil (**1e**) from which only **3e** was isolated in 50% yield after 1 hour of heating in ethylene glycol. The recovery of unreacted **1e** was nearly quantitative and none of **4e** seemed to be present in the reaction mixture.

The structures of **3** and **4** were readily established by spectroscopic and elemental analyses. One of the characteristic peaks in nmr spectra of **4** is the carbon-13 signal of bridge-head carbon atoms which usually appear at about 82 ppm [5]. Mass spectra of **3** also show peaks corresponding to molecular ions as base peaks. Other notable peak is at $M^+ - 28$ which correspond to the loss of carbon monoxide [11]. It has been reported that 2,4,5-triphenyloxazole (**3a**) shows peaks corresponding to fluorene radical ion and fluorenyl cation at m/z 166 and 165, respectively [12]. Formation of fluorene skeleton has been suggested as a results of rearrangements of 4-phenyl (60%) and 2-phenyl (40%) groups to C-5. In contrast to **3a**, triphenyloxazoles having substituents (**3b-g**) show that the fluorene radical ions are the major fragments and the fragments of fluorene cations are almost insignificant. Furthermore, both **3f** and **3g** show a fragment at m/z 210 which corresponds to a fluorene radical ion having a methyl and a methoxy group. These results are consistent with the migration of 2-aryl substituent to C-5. If a migration of 4-aryl group to C-5 takes place, peaks at m/z 194 and 226 would correspond to **3f** and **3g**, respectively.



fluorene radical ion fluorene cation

Reaction of *N*-methylurea (**2b**) with **1a** in ethylene glycol at 180° for 1 hour gave **3a** in 93% yield, which was the highest yield of the oxazole in current study. Benzoic acid was also isolated in 90% yield by acidifying the filtrate. None of the bicyclic compound of type **4** was isolated. *N*-Phenylurea (**2c**) also gave **3a** in 57% yield under the similar conditions. In addition, **6a** (50%) and ethylene glycol di(*N*-phenyl)carbamate was isolated in 30% yield. Although the yield of the carbamate was somewhat low, its isolation seemed to be an important clue in deducing the reaction mechanism (see below).

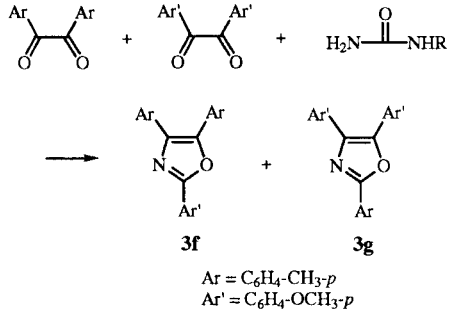
Formation of oxazole ring by various ring closures has been widely reviewed in literature [13]. One of the procedures that use urea (**2a**) is the reaction of aqueous ammonia with **1a-c** in sealed-tube at 170°, producing **3a-c** over 90% yield [14-16]. Urea may undergo self-disproportionation forming ammonia [17], which, in turn, may react with **1** to give oxazoles **3**. However, our results may rule out such possibility because the yield of **3a** was the highest when the reaction was carried out in ethylene glycol. It is unlikely that the disproportionation takes place much favorably in that solvent. On the contrary, such disproportionation would be taken place readily when urea is heated at a temperature as high as 220°. The major product of direct heating was **4a** even when the mole ratio of **1a** and **2a** was 1:3.5. Furthermore, if free ammonia was involved, formation of 2,4,5-triphenylimidazole is expected as the major product. However, we were not able to detect from the reaction in ethylene glycol.

Table 2
Mass Spectral Fragments of 2,4,5-Triphenyloxazoles (**3**) [a]

Compound	M+ (%)	M+ – CO	Fluorene	Others
3a	297 (100)	269 (27)	166 (43)	165 (85)
3b	339 (100)	311 (17)	194 (23)	179 (38), 178 (17)
3c	387 (100)	359 (7)	226 (30)	211 (23), 113 (12)
3d	387 (100)	359 (18)	226 (35)	211 (19), 113 (15)
3e [b]	537 (33)	509 (3)	326 (8)	429 (8), 426 (16), 424 (8)
	535 (100)	507 (10)	324 (16)	245 (30), 243 (32), 207 (23)
	533 (98)	505 (10)	322 (8)	165 (18), 164 (32), 163 (24)
	531 (35)	503 (4)		147 (17), 119 (33), 75 (50)
3f	355 (100)	327 (5)	210 (25)	195 (16), 179 (19), 178 (16)
3g	371 (100)	343 (11)	210 (34)	211 (16), 195 (19), 171 (7)

[a] At 70 eV and 200°. [b] Four peaks (M+ + 6, M+ + 4, M+ + 2, M+) are listed indicating the presence of three bromine atoms.

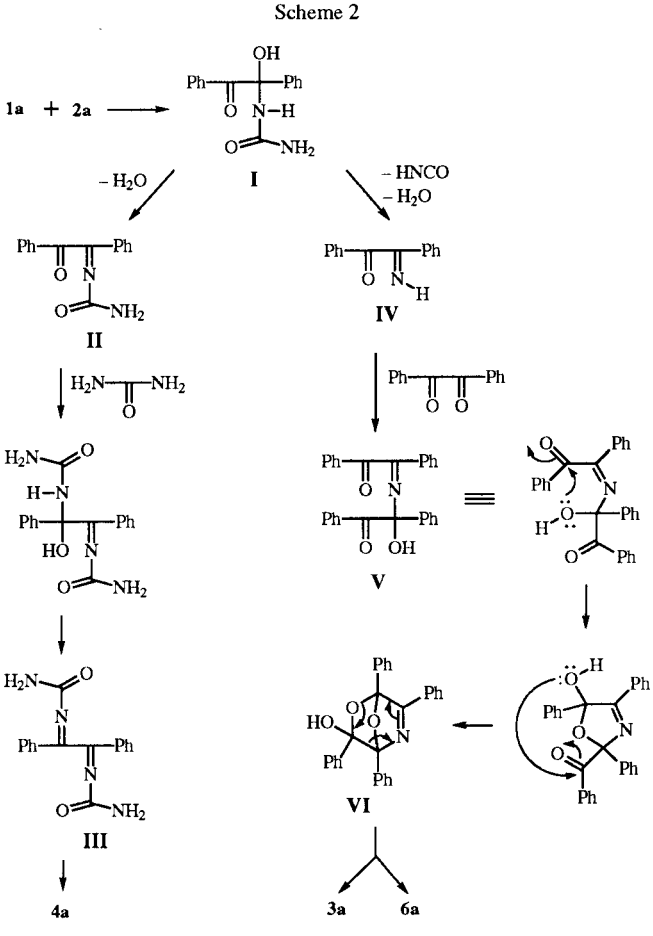
When a equimolar mixture of **1b** and **1c** was heated with **2a** in ethylene glycol for 2 hours all the four possible oxazoles, **3b**, **3c**, **3f**, and **3g** were isolated in about 2.8:1.3:1.4:1 (from isolated yields after column chromatography). Although the ratio may not be accurate, it is certain that the yield of **3b** is much greater than that of **3c**. This seems to be reasonable because of the electron-releasing nature of *p*-methoxy group in **1c** making the carbonyl group less susceptible to nucleophilic attack by urea.



Davidson *et al* [15] suggested a mechanism in which a benzilimide is involved in the formation of oxazole from **1a** and ammonia. An alternative mechanism was proposed by Wenkert *et al* [18] which implied a presence of a bicyclic intermediate. Based on our observation we propose a mechanism for the reaction of **1** and **2** leading to formation of **3** and **4**.

The key step may be the formation of an amido alcohol **I**. The amido alcohol may undergo dehydration to give benzilimide **II** which in turn will react further with urea to form benzildiimide **III**. The latter intermediate will undergo double cyclization to give compound **4**. On the other hand, the amido alcohol **I** will lose water and isocyanic acid component to form an α-iminoketone **IV**. The intermediate **IV** will react with a benzil **1** to form an imino alcohol **V** which may undergo double cyclization giving a bicyclic intermediate **VI**. A cycloreversion of **VI** will give **3** and **6**. The presence of the intermediate **IV** can readily explain the formation of cross-over products, **3f** and **3g**.

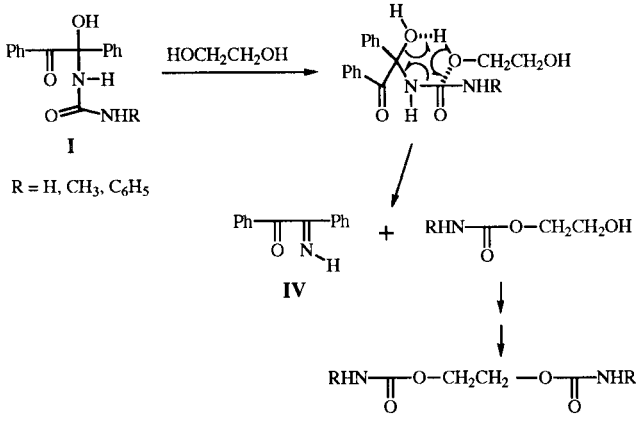
Scheme 2



As mentioned earlier, the yield of **3a** was highest when *N*-methylurea (**2b**) was used in ethylene glycol. Apparently, ethylene glycol may assist in the elimination of water and cyanic acid component by forming a carbamate derivative (Scheme 3). Although we did not attempt to isolate ethylene glycol bis(*N*-methyl)carbamate from

the reaction mixture, we were able to isolate ethylene glycol bis(*N*-phenyl)carbamate from the reaction mixture of **1a** and **2c**.

Scheme 3



EXPERIMENTAL

Melting points were determined on a MEL-TEMP apparatus and are uncorrected. Infrared (ir) spectra were recorded on a Perkin-Elmer Model 1430 spectrophotometer and the ultraviolet-visible (uv) spectra were recorded on a Hatachi U-3200 double beam spectrophotometer. Nuclear magnetic resonance (nmr) spectra were recorded on a JEOL-400 MHz FT spectrometer and chemical shifts were reported in parts per million (δ) relative to tetramethylsilane. Electron-impact mass spectra (ms) were obtained by Finigan MAT 95 spectrometer. Elemental analyses were performed by the M-H-W Laboratories, Phoenix, AZ.

Materials.

Benzils **1a-e**, ureas **2a-c**, and ethylene glycol were purchased from the Aldrich Chemical Co. and used without further purification.

Reaction of **1a** and **2a**.

2,4,5-Triphenyl-1,3-oxazole (**3a**) and 3a,6a-Diphenyltetrahydroimidazo[4,5-*d*]imidazole-2,5-dione (**4a**).

Heating in Ethylene Glycol.

A mixture of **1a** (2.00 g, 9.51 mmoles) and **2a** (2.0 g, 33.30 mmoles) in ethylene glycol (10 ml) was heated at 180° for 1 hour. A white solid was formed during the heating. The mixture was cooled to room temperature and the solid was collected by filtration. The residue was washed several times with ethyl ether and dried under vacuum to give a mixture of **3a** and **4a** (1.06 g, *ca.* 1:1 by nmr). The combined filtrate and wash were evaporated to remove the ether and then treated with water to develop cloudiness. White precipitate, which formed upon cooling in a refrigerator, was collected by filtration and recrystallized from ethanol to give **3a** (0.22 g, 15%), mp 115-116° (lit [14] 114-115°); ir (potassium bromide): 3056 (m), 1679 (w), 1598 (w), 1554 (w), 1497 (m), 1446 (m), 1079 (w), 1025 (2), 965 (m), 745 (ms), 709 (ms), 690 (vs) cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 7.38-7.49 (m, 6 H), 7.56 (m, 3 H), 7.65 (m, 4 H), 8.08 (m, 2 H); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 126.6, 126.9, 127.0, 128.1, 128.6, 128.9, 129.2, 129.4, 129.5, 129.7, 131.3, 132.3, 136.5, 145.7, 159.9; uv (ethanol): λ_{max} (ε) 229 nm (52000), 307 (49000), [lit [19] in methanol, 225 nm (log ε 4.41), 307 (4.38)]; ms: (70 eV) m/z (%) 297 (100, M^+), 269 (27), 166 (43), 165 (85).

Anal. Calcd. for $C_{21}H_{15}NO$ (297.36): C, 84.82; H, 5.08; N, 4.71. Found: C, 84.83; H, 5.24; N, 4.39.

The mixture of **3a** and **4a** was boiled in ethanol (300 ml) and the hot mixture was filtered. The filtrate gave **3a** (0.85 g, 60%, total yield of **3a** was 75%). The residue was mostly **4a** (0.31 g, 11%) which was recrystallized from dimethyl sulfoxide-ethanol (7:3 by volume) to give an analytically pure sample, mp >280° (lit [5] 300°); ir (potassium bromide): 3405 (s), 3050 (w), 1736 (vs), 1684 (vs), 1500 (s), 1460 (m), 1247 (w), 1144 (w), 1086 (w), 782 (s), 707 (s) cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 7.00-7.08 (m, 10 H), 7.75 (s, 4 H); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 82.3, 127.5, 127.8, 128.2, 138.7, 161.2; uv (ethanol): λ_{max} (ε) 259 nm (4800); ms: (70 eV) m/z (%) 294 (31, M^+), 251 (100), 147 (35), 121 (9), 104 (40), 77 (21).

Anal. Calcd. for $C_{16}H_{14}N_4O_2$ (294.32): C, 65.30; H, 4.79; N, 19.04. Found: C, 65.22; H, 4.83; N, 19.23.

Heating a Neat Mixture.

A mixture of **1a** (1.00 g, 4.75 mmoles) and **2a** (1.0 g, 16.65 mmoles) was heated in an oil-bath at 180° for 1 hour. The mixture became a clear solution in a few minutes and turned into a white solid mass. The solid was suspended in boiling ethanol (100 ml) for a few minutes and the hot mixture was filtered. The procedure was repeated three times and the residue was dried under vacuum to give **4a** (0.94 g, 67%). The ethanol wash gave **3a** (0.02 g, 3%) and benzoic acid (**6a**, 0.01 g, 3%).

Refluxing in Acetic Acid.

A mixture of **1a** (2.0 g, 9.51 mmoles), **2a** (2.0 g, 33.30 mmoles) and glacial acetic acid (10 ml) was heated at reflux for 1 hour. After cooling to room temperature, the mixture was filtered and the residue was washed with diethyl ether (30 ml). The residue was dried to give **4a** (1.16 g, 41%). The filtrate was treated with water (30 ml) to give a mixture of **1a**, **3a**, and **6a** (total 0.8 g). The mixture was dissolved in diethyl ether (50 ml), washed with saturated sodium bicarbonate solution (3 x 30 ml), dried, and evaporated to give **3a** (0.48 g, 34%). The aqueous extract was acidified with concentrated hydrochloric acid to give **6a** as a white solid (0.25 g, 43%).

2,4,5-Tri-(4-methylphenyl)-1,3-oxazole (**3b**) and 3a,6a-Di-(4-methylphenyl)tetrahydroimidazo[4,5-*d*]imidazole-2,5-dione (**4b**).

A mixture of **1b** (0.80 g, 3.36 mmoles), **2a** (0.48 g, 7.99 mmoles), and ethylene glycol (5 ml) was heated in an oil-bath at 180° for 2 hours. After cooling, the white solid was collected by filtration, washed with methanol, and dried under vacuum to give a mixture of **3b** and **4b** (0.44 g, 1.6:1 by nmr, which corresponded to 48% of **3b** and 15% of **4b**). The filtrate was concentrated and then treated with water to give a white solid. The solid was collected by filtration and recrystallized from ethanol to give **3b** (0.11 g, 19%), mp 147-148° (lit [14] 145°); ir (potassium bromide): 3042 (m), 2935 (m), 2870 (m), 1621 (w), 1575 (vw), 1530 (s), 1470 (m), 1175 (m), 1081 (m), 830 (vs), 742 (s) cm^{-1}; ^1H nmr (chloroform-d): δ 2.39 (s, 6 H, 4- and 5-$ArCH_3$), 2.41 (s, 3 H, 2-$ArCH_3$), an AA'BB' pattern centered at 7.18 and

7.20 (4 H, C_6H_4, J = 7.2 Hz), an AA'XX' pattern centered at 7.27 and 8.03 (4 H, C_6H_4, J = 7.8 Hz), an AA'BB' pattern centered at 7.57 and 7.61 (4 H, C_6H_4, J = 7.6 Hz); ^{13}C nmr (chloroform-d): δ 21.3, 21.4, 21.5, 124.8, 126.3, 126.3, 126.4, 127.9, 129.2, 129.3, 129.4, 129.8, 136.1, 137.6, 138.3, 140.4, 145.1, 160.0; uv (ethanol): λ_{max} (ε) 226 nm (18800), 240 (15800), 248 (13300), 290 infl (13600), 313 (17100); ms: (70 eV) m/z (%) 339 (100, M^+), 311 (17), 194 (23), 179 (38), 178 (17).

Anal. Calcd. for $C_{24}H_{21}NO$ (339.44): C, 84.92; H, 6.24; N, 4.13. Found: C, 84.59; H, 6.16; N, 4.14.

The mixture of **3b** and **4b** was boiled with methanol (100 ml) and filtered. The residue was recrystallized from dimethyl sulfoxide-methanol (3:7) to give **4b** as analytically pure sample, 0.15 g (14%), mp 280°; ir (potassium bromide): 3220 (broad s), 3030 (m), 2920 (w), 1710 (s), 1675 (vs), 1617 (w), 1502 (s), 1455 (m), 1110 (w), 821 (s) cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 2.09 (s, 6 H, CH_3), an AA'BB' pattern centered at 6.86 and 6.93 (8 H, C_6H_4, J = 7.8 Hz), 7.64 (s, 4 H, NH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 20.2, 81.4, 126.7, 127.7, 135.2, 136.5, 160.4; ms: (70 eV) m/z (%) 322 (58, M^+), 279 (100), 264 (19).

Anal. Calcd. for $C_{18}H_{18}N_4O_2$ (322.37): C, 67.06; H, 5.63; N, 17.38. Found: C, 66.96; H, 5.34; N, 17.59.

2,4,5-Tri-(4-methoxyphenyl)-1,3-oxazole (**3c**) and 3a,6a-Di-(4-methoxyphenyl)tetrahydroimidazo[4,5-*d*]imidazole-2,5-dione (**4c**).

Heating a Neat Mixture.

A mixture of **1c** (1.00 g, 3.70 mmoles) and **2a** (1.00 g, 16.65 mmoles) was heated at 180° for 3 hours. The solid mass was ground and then washed with water several times. The residue was dissolved in methanol (350 ml) by boiling and cooled to room temperature. The white precipitate was collected by filtration and dried under vacuum to give a mixture of **1c**, **3c**, and **4c** (1.08 g, 4.8:1:15.9 by nmr, which corresponded to 19%, 8%, and 63%, respectively). The solid mixture was redissolved in methanol (300 ml) and cooled slowly to give only **4c** as a white solid, 0.80 g (61%), mp 275°; ir (potassium bromide): 3210 (broad s), 2955 (w), 2822 (w), 1682 (s), 1611 (m), 1529 (m), 1501 (s), 1460 (m), 1250 (vs), 1180 (s), 1032 (s), 838 (s) cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 3.63 (s, 6 H, CH_3), an AA'BB' pattern centered at 6.65 and 6.98 (8 H, C_6H_4, J = 8.7 Hz), 7.62 (s, 4 H, NH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 58.5, 82.0, 113.2, 128.7, 130.9, 159.2, 161.0; ms: (70 eV) m/z (%) 354 (53, M^+), 312 (17), 311 (86), 310 (27), 192 (12), 177 (83), 151 (27), 150 (34), 135 (17), 134 (100), 133 (21), 119 (20), 103 (14), 91 (24).

Anal. Calcd. for $C_{18}H_{18}N_4O_4$ (354.37): C, 61.01; H, 5.12; N, 15.81. Found: C, 61.27; H, 5.35; N, 15.49.

Refluxing in Ethylene Glycol.

A mixture of **1c** (1.00 g, 3.70 mmoles), **2a** (1.00 g, 16.65 mmoles), and ethylene glycol (10 ml) was heated at 180° for 3 hours. After cooling to room temperature the precipitate was collected by filtration and washed with diethyl ether. The residue was a mixture of **1c** and **3c** (0.30 g, 1:1.5 by nmr, which corresponded to 10% and 29%, respectively). The filtrate gave a second product which was mostly **3c**. The filtrate was recrystallized from methanol to give analytically pure compound of **3c** (0.35 g, 49%), mp 139-142° (lit [14] 141°; ir (potassium bromide): 3010 (w), 2958 (w), 1613 (m), 1518 (ms), 1462 (w), 1440 (vw), 1421 (w), 1368 (w), 1325 (w), 1299 (m), 1249 (vs), 1172 (s), 1106 (s), 1054 (m), 1030 (m), 965 (w), 834 (m) cm^{-1}; ^1H nmr (chloroform-d): δ 3.84 (s, 6 H, CH_3), 3.87 (s, 3 H, CH_3), 6.92 (apparent t, 4 H, C_6H_4, J = 8.5 Hz), an AA'XX' pattern centered at 6.98 and 8.08 (4 H, C_6H_4, J = 9.5 Hz), an AA'BB' pattern centered at 7.58 and 7.64 (4 H, C_6H_4, J = 8.5 Hz); ^{13}C nmr (chloroform-d): δ 55.55, 55.59, and 55.62 (all OCH_3), 114.3 (CH), 114.4 (CH), 114.4 (CH), 120.6, 122.2, 125.5, 128.2, 128.3, 129.5, 135.3, 144.6, 159.6, 159.8, 159.9, 165.1; ms: (70 eV) m/z (%) 387 (100, M^+), 359 (7), 226 (30), 211 (23), 113 (12).

Anal. Calcd. for $C_{24}H_{21}NO_4$ (387.44): C, 74.40; H, 5.46; N, 3.62. Found: C, 74.36; H, 5.30; N, 3.88.

Refluxing in Glacial Acetic Acid.

A mixture of **1c** (1.00 g, 3.70 mmoles), **2a** (1.00 g, 16.65 mmoles), and glacial acetic acid (5 ml) was heated at reflux for 3 hours. During the period pale yellow solid formed. After cooling the solid mass was collected by filtration, washed with diethyl ether, and dried under vacuum to give a mixture of **1c**, **3c**, and **4c** (0.50 g, 5.4:1:2.7 by nmr, which corresponded to 26%, 10%, and 13%, respectively). The filtrate was treated with water to give a solid mass which was a mixture of **1c**, **3c**, and **4c** (0.21 g, 7.1: 2.9: 1 by nmr, which corresponded to 12%, 9%, and 2%, respectively). The third product from the filtrate was a mixture of **1c** and **3c** (0.12 g, 2.1:1 by nmr, which corresponded to 7% and 12%, respectively).

2,4,5-Tri-(3-methoxyphenyl)-1,3-oxazole (**3d**) and 3a,6a-Di-(3-methoxyphenyl)tetrahydroimidazo[4,5-*d*]imidazole-2,5-dione (**4d**).

A mixture of **1d** (1.00 g, 3.70 mmoles), **2a** (1.00 g, 16.65 mmoles), and ethylene glycol (10 ml) was heated in an oil-bath at 180° for 2 hours. The solution was cooled to room temperature and kept in a refrigerator overnight to give a white precipitate. The mixture was filtered and the residue was washed with diethyl ether. The residue was recrystallized from ethanol to give **4d** (0.36 g, 27%), mp 270°; ir (potassium bromide): 3220 (broad s), 2948 (m), 2830 (w), 1705 (vs), 1680 (vs), 1598 (ms), 1495 (s), 1460 (s), 1420 (ms), 1320 (m), 1262 (s), 1198 (m), 1180 (m), 1142 (ms), 1038 (s), 988 (m), 855 (w), 782 (s), 740 (m) cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 3.58 (s, 6 H, CH_3), 6.59-6.74 (m, 6 H, aromatic), 7.04 (apparent t, 2 H, J = 7.90 Hz), 7.72 (s, 4 H, NH); uv (ethanol): λ_{max} (ε) 236 nm (3200), 284 (2900); ms: (70 eV) m/z (%) 354 (22, M^+), 311 (31), 281 (12), 256 (6), 207 (40), 177 (21), 147 (20), 119 (32), 75 (100).

Anal. Calcd. for $C_{18}H_{18}N_4O_4$ (354.37): C, 61.01; H, 5.12; N, 15.81. Found: C, 61.22; H, 5.38; N, 15.52.

The filtrate gave **3d** as a white powder (0.72 g, 50%), mp 127°; ir (potassium bromide): 3005 (w), 2975 (vw), 2945 (vw), 2920 (vw), 2830 (w), 1620 (s), 1608 (s), 1583 (s), 1562 (s), 1500 (s), 1480 (s), 1460 (s), 1440 (s), 1380 (w), 1330 (s), 1305 (s), 1250 (vs), 1042 (s), 995 (m), 875 (m), 780 (m), 750 (m), 698 (m) cm^{-1}; ^1H nmr (chloroform-d): δ 3.76, 3.84, and 3.90 (all s, 3 H each, OCH_3), 6.88-7.70 (m, 12 H, aromatic); uv (ethanol): λ_{max} (ε) 236 nm (3200), 284 (2900); ms: (70 eV) m/z (%) 387 (100, M^+), 359 (15), 226 (40).

Anal. Calcd. for $C_{24}H_{21}NO_4$ (387.44): C, 74.40; H, 5.46; N, 3.62. Found: C, 74.58; H, 5.41; N, 3.55.

2,4,5-Tri-(4-bromophenyl)-1,3-oxazole (**3e**).

A mixture of **1e** (1.00 g, 2.72 mmoles), **2a** (1.00 g, 16.7 mmoles), and ethylene glycol (10 ml) was heated in an oil-bath at 180° for 1 hour. After cooling the precipitate was collected by fil-

tration and recrystallized from ethanol to give **3e** (0.32 g, 44%). The filtrate gave additional **3e** (0.04 g, 6%) upon treatment with water (total 50%), mp 194-196°; ir (potassium bromide): 3050 (vw), 1600 (m), 1518 (w), 1495 (m), 1489 (s), 1485 (s), 1400 (m), 1395 (m), 1070 (s), 1008 (s), 982 (s), 828 (vs), 810 (s) cm^{-1}; ^1H nmr (chloroform-d): an AA'BB' pattern centered at δ 7.59 and 7.66 (4 H, C_6H_4, J = 8.5 Hz), an AA'BB' pattern centered at 7.61 and 7.69 (4 H, C_6H_4, J = 9.5 Hz), an AA'BB' pattern centered at 7.78 and 8.03 (4 H, C_6H_4, J = 8.5 Hz); ^{13}C nmr (chloroform-d): δ 122.4, 122.8, 122.9, 125.0, 125.6, 125.7, 127.1, 127.7, 127.8, 129.3, 130.6, 131.7, 131.9, 131.9, 159.4; ms: (70 eV) m/z (%) 537 (33, M^+ + 6), 535 (100, M^+ + 4), 533 (98, M^+ + 2), 531 (35, M^+), 509 (3), 507 (10), 505 (10), 503 (4), 428 (8), 426 (16), 424 (8), 326 (8), 324 (15), 322 (9), 245 (30), 243 (32), 207 (23), 165 (18), 164 (32), 163 (24), 147 (17), 119 (33), 75 (50).

Anal. Calcd. for $C_{21}H_{12}Br_3NO$ (534.06): C, 47.23; H, 2.26; Br, 44.89; N, 2.62. Found: C, 47.50; H, 2.35; Br, 44.75; N, 2.38.

Disproportionation of **1b** and **1c**. Preparation of 2-(4-Methoxyphenyl)-4,5-di-(4-methylphenyl)-1,3-oxazole (**3f**) and 2-(4-Methylphenyl)-4,5-di-(4-methoxyphenyl)-1,3-oxazole (**3g**).

A mixture of **1b** (1.00 g, 4.20 mmoles), **1c** (1.13 g, 4.20 mmoles), **2a** (2.00 g, 33.30 mmoles), and ethylene glycol (10 ml) was heated in an oil-bath at 180° for 2 hours. The reaction mixture was cooled to room temperature and the precipitate was collected by filtration, washed with diethyl ether and water, successively. The residue was dried under vacuum to give a white solid mass (0.95 g, *ca.* 70%). Thin layer chromatography on silica gel with hexane-ethyl acetate (10:1 by volume) showed four spots whose R_f values were: **3b**, 0.58; **3f**, 0.37; **3g**, 0.27; **3c**, 0.15. A portion of the solid (0.30 g) was chromatographed on a column of silica gel (2.0 cm x 20 cm) prepared with hexane-ethyl acetate (10:1 by volume) and 5 ml portion of each fraction was collected. Fractions 2-4 gave **3b** (67 mg, 10%). Fraction 5 gave **3f** (3 mg, 4%), mp 123-124°; ir (chloroform solution): 3020 (vw), 2930 (vw), 2840 (vw), 1620 (m), 1530 (w), 1465 (w), 1450 (w), 1430 (w), 1318 (w), 1265 (vs), 1168 (m), 842 (m), 838 (m) cm^{-1}; ^1H nmr (chloroform-d): δ 2.38 (s, 3 H, CH_3), 2.39 (s, 3 H, CH_3), 3.885 (s, 3 H, OCH_3), an AA'XX' pattern centered at 6.98 and 8.08 (4 H, C_6H_4, J = 9.0 Hz), an AA'BB' pattern centered at 7.18 and 7.20 (4 H, C_6H_4, J = 6.0 Hz), an AA'BB' pattern centered at 7.55 and 7.60 (4 H, C_6H_4, J = 8.1 Hz); ^{13}C nmr (chloroform-d): δ 21.4, 21.4, 55.4, 114.2, 120.4, 126.4, 126.5, 128.0, 128.1, 129.2, 129.3, 129.9, 136.1, 137.8, 138.3, 144.9, 159.9, 161.3; ms: (70 eV) m/z (%) 355 (100, M^+), 327 (5), 210 (25), 195 (16), 179 (19), 178 (16), 119 (19), 91 (13).

Anal. Calcd. for $C_{24}H_{21}NO_2$ (355.44): C, 81.10; H, 5.96; N, 3.94. Found: C, 81.36; H, 5.82; N, 3.89.

Fractions 7-8 gave **3g** as white powder (0.02 g, 20%), mp 123-124°; ir (chloroform solution): 3020 (vw), 2970 (vw), 2840 (vw), 1622 (w), 1531 (s), 1465 (w), 1310 (w), 1263 (vs), 1172 (m), 1102 (w), 1030 (m), 838 (vs) cm^{-1}; ^1H nmr (chloroform-d): δ 2.42 (s, 3 H, CH_3), 3.85 (s, 6 H, OCH_3), an AA'BB' pattern centered at 6.91 and 6.93 (4 H, C_6H_4, J = 5.5 Hz), an AA'BB' pattern centered at 7.59 and 7.64 (4 H, C_6H_4, J = 8.9 Hz), an AA'XX' pattern centered at 7.27 and 8.02 (4 H, C_6H_4, J = 8.5 Hz); ^{13}C nmr (chloroform-d): δ 21.5, 55.3, 55.3, 114.0, 114.1, 121.8, 124.9, 125.3, 126.3, 128.0, 129.3, 129.4, 135.2, 140.4, 144.7, 159.4, 159.7, 159.8; ms: (70 eV) m/z (%) 371 (100, M^+), 343 (11), 211 (16), 210 (34), 195 (19), 171 (7).

Anal. Calcd. for $C_{24}H_{21}NO_3$ (371.44): C, 77.61; H, 5.70; N, 3.77. Found: C, 77.87; H, 5.60; N, 3.77.

Fractions 11-14 gave **3c** (26 mg, 3%).

Reaction of **1a** and **2b**.

A mixture of **1a** (1.00 g, 4.76 mmoles) and **2b** (1.00 g, 13.50 mmoles) in ethylene glycol (10 ml) was heated at 180° for 1 hour. After cooling the precipitate was collected by filtration, washed with water and then recrystallized from ethanol to give **3a** (0.66 g, 93%), mp 114-118°. The ethylene glycol filtrate and wash were combined and acidified with concentrated hydrochloric acid to give **6a** (0.26 g, 90%).

Reaction of **1a** and **2c**.

Similar reaction was carried out with **1a** (1.00 g, 4.76 mmoles) and **2c** (1.30 g, 9.51 mmoles) in ethylene glycol (10 ml) to give **3a** (0.41 g, 58%). The filtrate was acidified with concentrated hydrochloric acid and the resulting precipitate was collected and chromatographed on a column of silica gel with hexane-ethyl acetate (10:1) to isolate additional **3a**, **6a**, and ethylene glycol bis(*N*-phenyl)carbamate.

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