Formation of Acyl-Substituted Nitrile Ylides by $Rh_2(OAc)_4$-Catalyzed Decomposition of α-Diazocarbonyl Compounds in Nitriles

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The $Rh_2(OAc)_4$-catalyzed reactions of α-diazocarbonyl compounds in nitrile in the presence of dimethyl acetylenedicarboxylate (DMAD) gave oxazole and pyrrole derivatives. The formation of the oxazole derivatives is explained in terms of the 1,5-cyclization of an acyl-substituted nitrile ylide intermediate, and the formation of the pyrrole derivatives is explained by the 1,3-dipolar cycloaddition of the same intermediate with DMAD. The regiochemistry of the cycloaddition of the acyl-substituted nitrile ylide with methyl propiolate showed that the contribution of an allenyl-type resonance structure plays an important role in the acyl-substituted nitrile ylide reaction.

Nitrile ylide has long been viewed as one of the most attracting chemical species from synthetic and theoretical points of view. In 1961, Huisgen first reported the generation of the nitrile ylide intermediate by hydrogen chloride elimination from an imidoyl chloride.[1] After this pioneering work, several methods of generating the nitrile ylide have been developed:[2] carbon dioxide extrusion from oxazolin-5-ones, alkyl phosphate extrusion from oxazaphosphole derivatives, addition of triphenylborane to isocyanides, photochemical ring opening of 2*H*-azirines, and isocyanide extrusion from 3-imino-1-azetines. In 1982, Kende et al. reported the generation of nitrile ylide by the carbene-nitrile reaction.[3] Although this reaction has been extensively investigated as a new route to nitrile ylide,[4] no report has been published on the formation of acyl-substituted nitrile ylide.

The catalytic decomposition of α-diazocarbonyl compounds in nitrile was reported by Huisgen and his coworkers in 1961 to give oxazole derivatives.[5] They explained the oxazole formation by the concerted 1,3-dipolar cycloaddition of ketocarbene with nitrile. Since the discovery of the carbene-nitrile reaction, the stepwise mechanism including the intermediacy of the acyl-substituted nitrile ylide has been pointed out in this oxazole synthesis. However, there has been no evidence of the intermediate, because of its facile 1,5-cyclization to give the oxazole ring.

Here we report direct evidence of the acyl-substituted nitrile ylide intermediate by a trapping experiment with dimethyl acetylenedicarboxylate (DMAD).

Results and Discussion

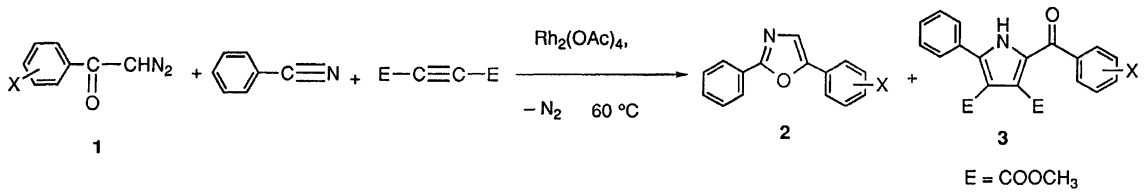
The $Rh_2(OAc)_4$-catalyzed decomposition of *p*-chloro-α-diazoacetophenone (**1f**) in the presence of dimethyl acetylenedicarboxylate (DMAD) in benzonitrile at 60 °C gave 5-(*p*-chlorophenyl)-2-phenyloxazole (**2f**) and dimethyl 2-(*p*-chlorobenzoyl)-5-phenylpyrrole-3,4-dicarboxylate (**3f**) in 63 and 11% yields, respectively.

The structure of pyrrole derivative **3f** was determined from elemental analysis and spectroscopic data: The ^{1}H NMR spectrum shows two signals from methoxy groups at 3.44 and 3.73 ppm, and a broad N–H signal at 10.09 ppm. The IR spectrum shows the presence of an N–H group at 3327 cm^{-1}, an ester-carbonyl group at 1725 cm^{-1}, and a keto-carbonyl group at 1621 cm^{-1}. The ^{13}C NMR spectrum shows the presence of three carbonyl carbons (at 163.59, 164.90, and 185.19 ppm), and four sp^2 carbons in a pyrrole ring (at 113.82, 125.06, 128.12, and 140.46 ppm as doublet signals by coupling with an N–H proton).

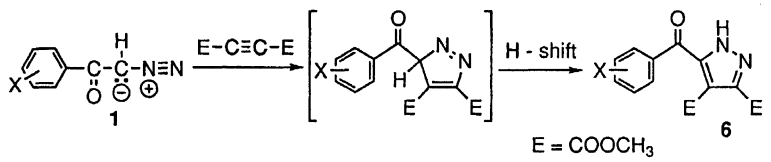
The reactions of *p*-, *m*-, and *o*-substituted α-diazoacetophenones also gave the corresponding oxazole derivatives **2** and pyrrole derivatives **3** in the yields listed in Table 1 (Scheme 1). While electron-withdrawing groups afforded **2** and **3** in moderate yields (Runs e—i), electron-releasing substituents decreased the total yield (**2**+**3**) (Runs a—c), which is attributed to the side reaction with DMAD to give pyrazole **6** (**6a**: 25%, **6b**: 8.9%) (Scheme 2).

The treatment of *o*-substituted α-diazoacetophenones **1j** and **1k** resulted in the formation of **2** or **3** in low yields, since their substituents at the *o*-position sterically hindered the formation of the nitrile ylide.

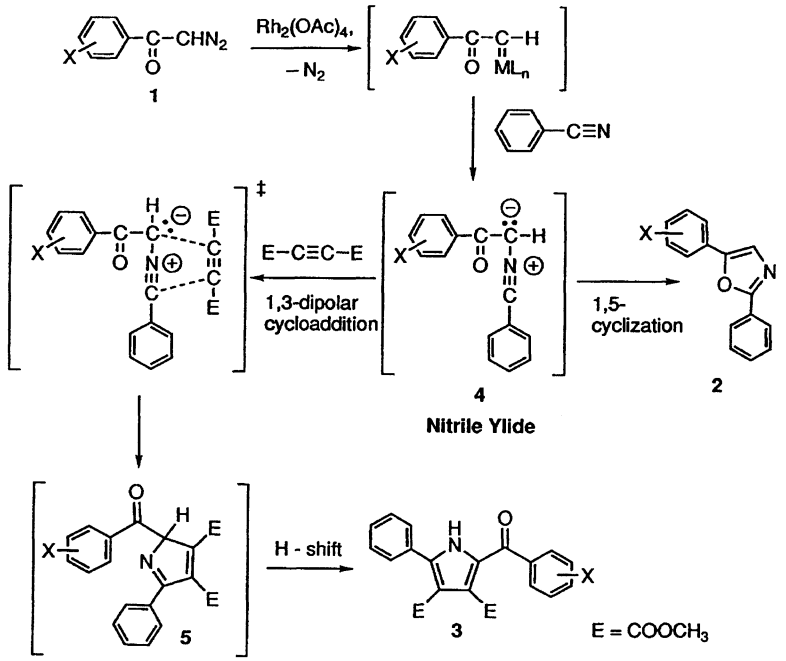
The formation of oxazole **2** and pyrrole **3** can be rationalized by a stepwise mechanism (Scheme 3). The reaction of rhodium carbenoid with benzonitrile gave acyl-substituted nitrile ylide intermediate **4**, which gave



Scheme 1.



Scheme 2.



Scheme 3.

Table 1. Substituent Effects on the Yields and Ratios of Oxazole **2** and Pyrrole **3** in the $Rh_2(OAc)_4$-Catalyzed Reaction of α-Diazoacetophenones with Benzonitrile in the Presence of DMAD[a)]

Run	X	Yield/%		Total yield/%	Ratio
		2	**3**	**2+3**	**3/2+3**
a	*p*-OMe	38.2	5.8	44.0	0.13
b	*m*-Me	32.0	2.0	34.0	0.06
c	*p*-Me	44.6	9.8	54.4	0.18
d	H	50.6	11.0	61.6	0.18
e	*m*-Cl	62.6	15.1	77.7	0.19
f	*p*-Cl	63.0	11.0	74.0	0.15
g	*p*-CN	60.9	9.0	69.9	0.13
h	*m*-NO_2	60.5	12.5	73.0	0.17
i	*p*-NO_2	61.2	18.3	79.5	0.23
j	*o*-Me	3.0	0.0	3.0	0.00
k	*o*-Cl	9.0	1.5	10.5	0.14

a) Reactions were carried out in the presence of 5 mol% of $Rh_2(OAc)_4$ and 20 molar amounts of DMAD.

oxazole **2** by intramolecular 1,5-cyclization. On the other hand, intermolecular 1,3-dipolar cycloaddition of **4** with DMAD gave rise to the corresponding cycloadduct **5**, which produced pyrrole derivative **3** by subsequent aromatization through 1,5-hydrogen migration. The isolation of pyrrole **3** indicates the stepwise mechanism of the formation of oxazole **2** through the nitrile ylide intermediate.

The reaction of **2** with DMAD, a so-called abnormal Diels–Alder reaction,[6—9)] can be considered as another possible route to **3**. In the present case, however, the pathway through the abnormal Diels–Alder reaction was completely excluded by a control experiment in which 5-(*p*-chlorophenyl)-2-phenyloxazole (**2f**) was treated with DMAD under the same conditions to give no pyrrole **3f** and quantitative recovery of **2f**.

Solvent effects on the reactivity of nitrile ylide intermediate **4f** were studied using various nonpolar and polar solvents (Table 2). Reactions in runs a—g show that

Table 2. Solvent Effects on the Yields and Ratios of **2f** and **3f**

Run	Solvent (Dielectric constant)	Yield/%		Total yield/%	Ratio
		2f	**3f**	**2f+3f**	**3f/2f+3f**
a	CCl_4 (2.24)	48.6	2.4	51.0	0.05
b	C_6H_6 (2.27)	38.3	2.0	40.3	0.05
c	$CHCl_3$ (4.81)	33.6	4.4	38.0	0.12
d	C_6H_5Cl (5.02)	45.4	2.8	48.2	0.06
e	$CH_3COOC_2H_5$ (6.0)	10.8	0.8	11.6	0.07
f	o-$Cl_2C_6H_4$ (9.93)	41.3	3.8	45.1	0.08
g	C_6H_5CN (25.20)	63.0	11.0	74.0	0.17
h	THF (7.58)	0.0	3.5	3.5	1.00
i	DMF (36.71)	0.0	0.0	0.0	—
j	DMSO (46.68)	0.0	0.0	0.0	—

pyrrole derivative **3f** increased with increasing solvent polarity. This trend can be explained by the stabilization of the nitrile ylide intermediate by the polar media to reduce the intramolecular 1,5-cyclization leading to oxazole **2f**. The reactions in polar solvents such as DMF and DMSO showed a color change of $Rh_2(OAc)_4$ from green to blue or wine red, respectively, affording neither the oxazole or pyrrole derivative. This is attributed to the deactivation of the catalyst by the coordination of these solvent molecules to the catalyst active site.

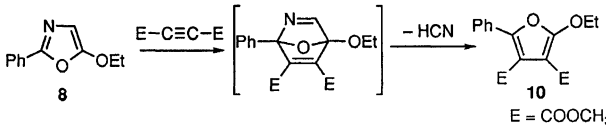
In contrast to the reactions of α-diazoacetophenone, catalytic decomposition of α-diazoacetates (**7**) with $Rh_2(OAc)_4$ in acetonitrile in the presence of DMAD did not give the corresponding oxazole derivatives (**8**), but gave pyrroles **9a—c** in low yields (Table 3, Runs a—c). This may be ascribed to the side-reaction of carbenoid or nitrile ylide with DMAD, since oxazole **8c** was obtained in an 80.6% yield in the reaction of p-nitrophenyl diazoacetate with acetonitrile in the absence of DMAD, and **8c** was stable under the reaction conditions (Scheme 4).

The treatment of ethyl diazoacetate with benzonitrile in the presence of DMAD afforded the corresponding oxazole **8d** and pyrrole **9d** along with dimethyl 2-ethoxy-5-phenylfuran-3,4-dicarboxylate (**10**) (Table 3, Run d). The formation of the products is explained by a mechanism similar to the case of α-diazoacetophenones. Furan **10d** may be formed by the reaction of oxazole **8d** with DMAD (Scheme 5), because of the activation by the ethoxyl group on the 5-position. The bulky t-butyl group hinders the intermolecular reaction giving **9e**, increasing the yield of **8e** (Table 3, Run e). In Runs d—f, higher ratios of the yield of **9**/total (0.33—0.71) were observed than in the case of the α-diazoacetophenones (<0.23).

Table 3. The $Rh_2(OAc)_4$-Catalyzed Reaction of α-Diazoacetates with Nitrile in the Presence of DMAD[a)]

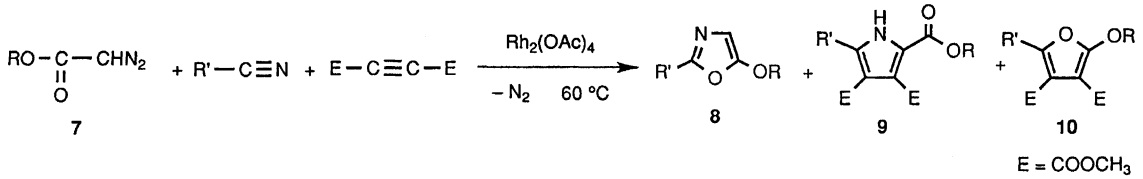
Run	R	R′	Yield/%		Total yield/%	Ratio
			8	**9**	**8+9**	**9**/total
a	Et	Me	—	12.6	12.6	—
b	^{t}Bu	Me	—	7.4	7.4	—
c	p-$NO_2C_6H_4$	Me	—	11.9	11.9	—
d	Et	Ph	4.8	17.8	25.2[b)]	0.71[c)]
e	^{t}Bu	Ph	8.7	11.2	19.9	0.56
f	p-$NO_2C_6H_4$	Ph	28.0	13.9	41.9	0.33

a) Reactions were carried out in the presence of 5 mol% of $Rh_2(OAc)_4$ and 20 molar amounts of DMAD. b) 2.6% of furan **10** was obtained. c) Including furan **10**.

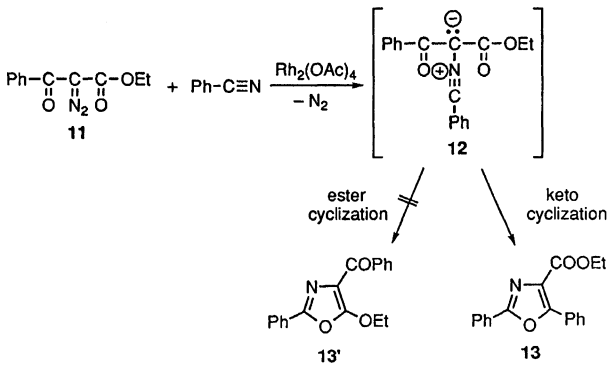


Scheme 5.

In order to compare the cyclization facility of the keto- and ester-carbonyl groups, ethyl diazobenzoylacetate (**11**) was treated under similar conditions in the presence of benzonitrile, and the corresponding oxazole **13** was obtained as a sole cyclization product of nitrile ylide **12** in a 6% yield (Scheme 6). Absorption of the carbonyl group at 1724 cm^{-1} in the IR spectrum and a signal at 162.32 ppm in the ^{13}C NMR spectrum showed the presence of an ester group in product **13**. This indicates that in nitrile ylide intermediate **12**, the keto-carbonyl group cyclizes predominantly to give ethyl 2, 5-diphenyloxazole-4-carboxylate (**13**) without affording 5-ethoxyoxazole **13′** through cyclization of the ester-carbonyl group. Therefore, this intramolecular com-



Scheme 4.



Scheme 6.

petition implies the slow intramolecular 1,5-cyclization of the alkoxycarbonyl-substituted nitrile ylide to afford the oxazole derivative.

In order to determine the substituent effect of the nitrile carbon on the reactivity of the nitrile ylide, catalytic reactions of *p*-nitro-α-diazoacetophenone (**1i**) with various nitriles were carried out in the presence of 20 molar amounts of DMAD at 60 °C (Table 4).

The reactions with pentafluorobenzonitrile and phenylcyanate gave only oxazole **14a** and **14b** in moderate yields without affording the pyrrole derivative at all (Scheme 7). Although the reactions of dimethyl- and diethylcyanamide resulted in complex mixtures, diisopropylcyanamide gave the corresponding oxazole **14e** and pyrrole **15e** in high yields, because the bulky isopropyl groups may hinder the side reaction of cyanamide with DMAD. In this reaction, however, no significant effect of heteroatom substitution to accelerate the 1,3-dipolar cycloaddition of the nitrile ylide intermediate was recognized in comparison with the reaction of benzonitrile (Table 1, Run i).

The regiochemistry of the cycloaddition of the nitrile ylide with unsymmetrical dipolarophiles has been discussed by many chemists. The cycloaddition of nitrile ylide is known to be controlled by the HOMO of the ylide and the LUMO of the dipolarophiles, and is accelerated by electron-withdrawing groups on the dipolarophile.[10] In two possible transition states, most nitrile ylides react via **TA** to give 4-substituted cycloadducts (**PA**) regioselectively (Fig. 1).

Although successful trapping experiments of the acyl-substituted nitrile ylide have been reported by a few groups, the regiochemistry of the cycloaddition with unsymmetrical dipolarophiles has not been discussed sufficiently. Hirai and Fehlhammer reported the reaction of acyl-substituted nitrile ylide with an unsymmetrical dipolarophile to give a pyrroline derivative through a **TB**-type transition state (Fig. 2) without affording the normal product through **TA**.[11,12] These results may be explained by the strong perturbation on the nitrile ylide due to the strained four-membered ring or the effect of the substituted platinum metal.

In order to clarify the regiochemistry of 1,3-dipolar cycloaddition of acyl-substituted nitrile ylides, $Rh_2(OAc)_4$-catalyzed decomposition of *p*-nitro-α-diazoacetophenone (**1i**) was carried out in the presence of 20 molar amounts of methyl propiolate in benzonitrile.

Table 4. The $Rh_2(OAc)_4$-Catalyzed Reaction of **1i** with Various Nitriles in the Presence of DMAD[a]

Run	R	Yield/%		Total yield
		14	**15**	%
a	C_6F_5	58	0	58
b	C_6H_5O	63	0	63
c	Me_2N	0	0	0
d	Et_2N	12	0	12[b]
e	$^iPr_2N$	71	8	79

a) Reactions were carried out in the presence of 5 mol% of $Rh_2(OAc)_4$ and 20 molar amounts of DMAD in an excess of nitrile. b) 0.5% of **16** was obtained.

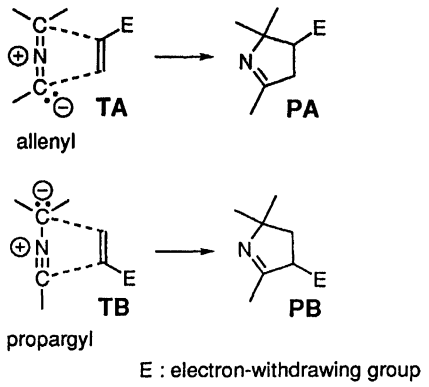


Fig. 1.

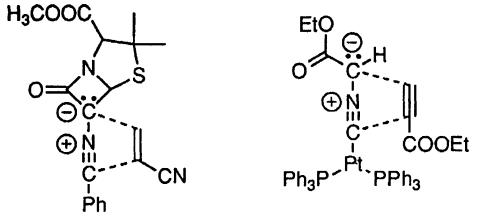
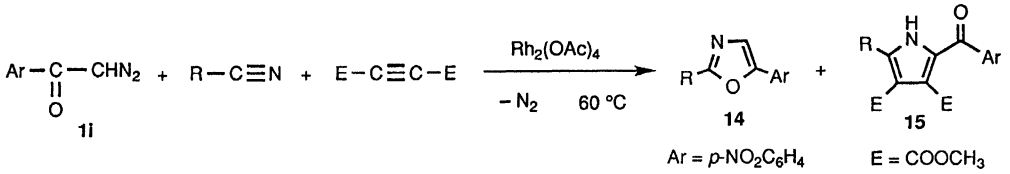


Fig. 2.



Scheme 7.

This reaction yielded oxazole **17a** and pyrrole **18a** in 70 and 4% yields, respectively (Table 5 and Scheme 8). The structure of **18a** was elucidated by the results of differential NOE experiments (Fig. 3) which showed enhancement of the ortho-proton intensity on the phenyl group by the irradiation onto H-4 on the pyrrole ring at 7.05 ppm. Similar reactions in acetonitrile and diisopropylcyanamide also gave the corresponding pyrrole derivatives. The major pyrrole derivatives **18b** and **18c** were determined to have the same regiochemistry as **18a**.

The structure of the main adduct **18** indicates that the cycloaddition is considered to proceed through a **TA**-type transition state, in which the nitrile ylide is depicted as an allenyl structure (Scheme 9). These results show that the regiochemistry of the 1,3-dipolar cycloaddition of the acyl-substituted nitrile ylide having no extra perturbation toward an unsymmetrical dipolarophile was essentially the same as the regiochemistry of alkyl- or aryl-substituted nitrile ylides, contrary to the results of Hirai and Fehlhammer. Consequently, the electronic effect of the acyl group on the reactivity of nitrile ylide is not so large, and its reaction is controlled by the electronic properties of an allenyl-type ylide moiety.

Table 5. The $Rh_2(OAc)_4$-Catalyzed Decomposition of **1i** in Various Nitriles in the Presence of Methyl Propiolate[a)]

Run	R	Yield/%		
		17	**18**	**19**
a	Ph	70	4	0
b	CH_3	73	4	1
c	$^iPr_2N$	90	5	0

a) Reactions were carried out in the presence of 5 mol% of $Rh_2(OAc)_4$ and 20 molar amounts of DMAD.

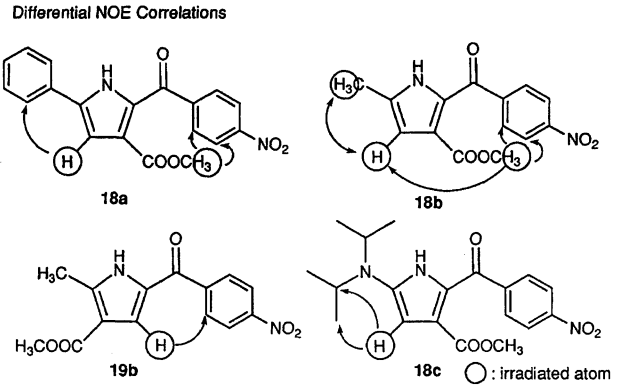


Fig. 3. Differential NOE Correlations of **18a**, **18b**, **19b**, and **18c**.

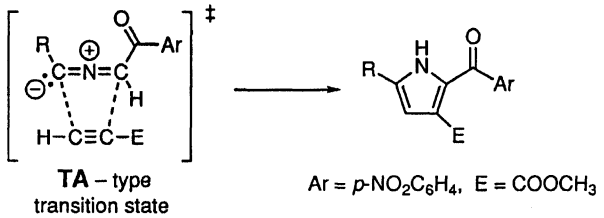
Experimental

Melting points were measured with a Yanagimoto melting-point apparatus and were not corrected. IR spectra were recorded on a Perkin–Elmer model 983. ^1H NMR (270.05 MHz) and ^{13}C NMR (67.8 MHz) spectra were recorded on a JEOL EX-270 in $CDCl_3$ solution using TMS as an internal standard. Mass spectra were determined with a JEOL JMS-DX303 spectrometer and a Shimadzu GCMS-QP2000A gas chromatograph mass spectrometer. Elemental analyses were performed on a Yanaco CHN corder MT-5.

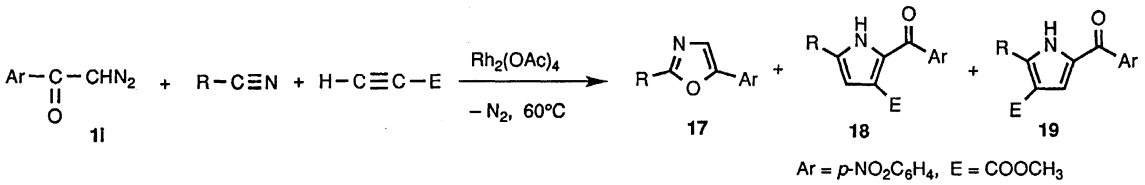
Materials and Solvents. α-Diazoacetophenones were prepared by the reaction of the corresponding acid chlorides with an excess of diazomethane in the presence of triethylamine according to Newman's method.[13)] Ethyl diazoacetate was prepared by the diazotization of ethyl glycinate hydrochloride with sodium nitrite.[14)] *t*-Butyl diazoacetate was prepared by the acyl cleavage of *t*-butyl diazoacetoacetate with sodium methoxide.[15)] *p*-Nitrophenyl diazoacetate was prepared by the reaction of the *p*-nitrophenyl chloroformate with an excess of diazomethane in the presence of triethylamine.[16)] Benzonitrile was purified by distillation after reflux on P_2O_5. Acetonitrile was purified by distillation after reflux on CaH_2. Other solvents were dried by appropriate methods and distilled just before use. DMAD was purified by distillation of the commercial reagent.

General Procedure for the $Rh_2(OAc)_4$-Catalyzed Decomposition of Diazocarbonyl Compound in the Presence of Nitrile and DMAD. A solution of diazocarbonyl compound (1.0 mmol) in 20 ml of nitrile was added dropwise to a solution of $Rh_2(OAc)_4$ (22.1 mg, 5.0×10^{-2} mmol) and dimethyl acetylenedicarboxylate (20.0 mmol) in 10 ml of nitrile for 2 h under nitrogen atmosphere at 60 °C. After heating for an additional hour, the solution was concentrated under reduced pressure and separated by medium pressure liquid chromatography (silica gel, eluted with ethyl acetate–hexane).

The $Rh_2(OAc)_4$-catalyzed reaction of *p*-methoxy-α-di-



Scheme 9.



Scheme 8.

azoacetophenone (**1a**) with benzonitrile in the presence of DMAD gave **2a**, **3a**, and **6a**.

5-(*p*-Methoxyphenyl)-2-phenyloxazole (2a): 38.2% yield; colorless crystals; mp 81.7—83.3 °C (from hexane); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=3.84 (3H, s, OCH_3), 6.96 (2H, d, J=8.9 Hz, arom-H), 7.31 (1H, s, 4-H), 7.41—7.51 (3H, m, arom-H of Ph), 7.64 (2H, d, J=8.9 Hz, arom-H), and 8.06—8.10 (2H, m, arom-H of Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=55.29 (q, OCH_3), 114.36 (dd, $^3J_{CH}$=4.9 Hz, 3″-arom-CH), 120.85 (t, $^3J_{CH}$=7.9 Hz, 1″-arom-C), 121.92 (d, J_{CH}=192.6 Hz, 4-CH), 125.69 (dd, $^3J_{CH}$=7.3 Hz, 2″-arom-CH), 126.09 (dm, 2′-arom-CH of Ph), 127.56 (m, 1′-arom-C of Ph), 128.72 (dm, 3′-arom-CH of Ph), 130.03 (dt, $^3J_{CH}$= 7.6 Hz, 4′-arom-C of Ph), 151.27 (dt, $^2J_{CH}$=16.8 Hz, $^3J_{CH}$= 4.3 Hz, 5-C), 159.78 (m, 4″-arom-C), and 160.50 (m, 2-C); IR (KBr) 2919, 2840, 1730, 1697, 1611, 1565, 1540, 1498, 1460, 1447, 1299, 1290, 1279, 1256, 1176, 1128, 1111, 1059, 1026, 951, 934, 826, 774, 707, 689, and 669 cm^{-1}; MS (EI) 252, 251 (M^+), 236, 208, 196, 181, 165, 153, 135, 126, 112, 89, and 77. Found: C, 76.63; H, 5.31; N, 5.51%. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57%.

Dimethyl 2-(*p*-Methoxybenzoyl)-5-phenylpyrrole-3,4-dicarboxylate (3a): 5.8% yield; colorless crystals; mp 206.9—209.0 °C (from benzene–hexane); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=3.48 (3H, s, $COOCH_3$), 3.73 (3H, s, $COOCH_3$), 3.88 (3H, s, OCH_3), 6.95 (2H, d, J=8.9 Hz, arom-H), 7.45—7.47 (3H, m, arom-H of Ph), 7.59—7.63 (2H, m, arom-H of Ph), 7.75 (2H, d, J=8.9 Hz, arom-H), and 9.76 (1H, brs, N-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=51.76 (q, $COO\underline{C}H_3$), 52.17 (q, $COO\underline{C}H_3$), 55.52 (q, OCH_3), 113.53 (d, $^3J_{CH}$=7.3 Hz, 4-C), 113.65 (dd, $^3J_{CH}$=4.9 Hz, 3″-CH of Ar), 124.13 (d, $^3J_{CH}$=6.1 Hz, 3-C), 128.43 (dt, $^3J_{CH}$=3.7 Hz, 2′-CH of Ph), 128.95 (d, $^2J_{CH}$=3.1 Hz, 2-C), 129.11 (dm, 3′-CH of Ph), 129.52 (dt, $^3J_{CH}$=7.9 Hz, 4′-CH of Ph), 129.98 (m, arom-C), 130.49 (m, arom-C), 131.05 (dd, $^3J_{CH}$=6.7 Hz, 2″-CH of Ar) 139.69 (d, $^2J_{CH}$=4.3 Hz, 5-C), 163.38 (m, 4″-C of Ar), 163.91 (m, $\underline{C}OOCH_3$), 165.24 (m, $\underline{C}OOCH_3$), and 185.28 (m, C=O); IR (KBr) 3298 (NH), 2954, 1719 (ester-C=O), 1616 (keto-C=O), 1598, 1566, 1508, 1482, 1460, 1443, 1432, 1418, 1299, 1242, 1198, 1170, 1143, 1089, 1016, 971, 922, 858, 839, 796, 760, 698, and 668 cm^{-1}; MS (EI) 394, 393 (M^+), 362, 361, 331, 330, 302, 287, 275, 254, 181, 165, 135, 107, 92, and 77. Found: C, 67.91; H, 4.93; N, 3.59%. Calcd for $C_{22}H_{19}NO_6$: C, 67.17; H, 4.87; N, 3.56%.

Dimethyl 5-(*p*-Methoxybenzoyl)pyrazole-3,4-dicarboxylate (6a): 24.8% yield; colorless crystals; mp 146.7—148.7 °C (from benzene–hexane); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=3.85 (3H, brs, $COOCH_3$), 3.89 (3H, s, $COOCH_3$ or OCH_3), 3.97 (3H, s, $COOCH_3$ or OCH_3), 6.98 (2H, d, J=8.9 Hz, 3′-H of Ar), 8.15 (2H, br d, J=8.9 Hz, 2′-H of Ar), and 11.25 (1H, brs, NH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=52.86 (q, $COO\underline{C}H_3$), 52.99 (q, $COO\underline{C}H_3$), 55.54 (q, OCH_3), 113.82 (dd, $^3J_{CH}$=4.88 Hz, 3′-CH of Ar), 118.82 (s, 4-C), 128.91 (t, $^3J_{CH}$=7.93 Hz, 1′-C of Ar), 132.66 (dd, $^3J_{CH}$=7.33 Hz, 2′-CH of Ar), 135.33 (brs, 5-C), 147.96 (s, 3-C), 159.32 (q, $^3J_{CH}$=3.67 Hz, $\underline{C}OOCH_3$), 163.60 (q, $^3J_{CH}$=4.27 Hz, $\underline{C}OOCH_3$), 164.14 (m, 4′-C of Ar), and 184.51 (t, $^3J_{CH}$=4.27 Hz, C=O); IR (KBr) 3255 (NH), 2960, 2849, 1744 (ester-C=O), 1640 (keto-C=O), 1604, 1577, 1511, 1483, 1447, 1382, 1311, 1286, 1250, 1217, 1182, 1168, 1100, 1046, 1009, 965, 913, 838, 821, 806, 790, 774, 762, and 669 cm^{-1}; MS (EI) 320, 319 (MH^+), 288, 287, 256, 229, 228, 227, 226, 201, 200, 199, 198, 171, 144, 136, 135, 107, 92, 77. Found: C, 56.41; H, 4.46; N, 8.73%. Calcd for $C_{15}H_{14}N_2O_6$: C, 56.60; H, 4.43; N, 8.80%.

The $Rh_2(OAc)_4$-catalyzed reaction of *m*-methyl-α-diazoacetophenone (**1b**) with benzonitrile in the presence of DMAD gave **2b** and **3b**.

5-(*m*-Methylphenyl)-2-phenyloxazole (2b): 32.0% yield; colorless crystals; mp 111.4—113.2 °C (from hexane); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=2.41 (3H, s, CH_3), 7.15 (1H, d, J=7.9 Hz, 6″-H of Ar), 7.32 (1H, t, J=7.9 Hz, 5″-H of Ar), 7.42 (1H, s, 4-H), 7.44—7.53 (5H, m, arom-H), and 8.09—8.13 (2H, m, arom-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=21.46 (qt, $^3J_{CH}$=4.9 Hz, CH_3), 121.39 (dt, $^3J_{CH}$=7.3 Hz, 6″-CH of Ar), 123.34 (d, J_{CH}=192.3 Hz, 4-CH), 124.78 (dm, arom-CH), 126.27 (dm 2′-CH of Ph), 127.51 (m, 1′-C of Ph), 127.92 (d, 1″-C of Ar), 128.80 (dd, 3′-CH of Ph), 128.84 (dd, 5″-CH of Ar), 129.27 (dm, arom-CH), 130.27 (dt, $^3J_{CH}$=7.3 Hz, 4′-CH of Ph), 138.64 (m, 3″-C of Ar), 151.42 (dt, $^2J_{CH}$=17.0 Hz, $^3J_{CH}$=4.3 Hz, 5-C), and 161.05 (dt, $^3J_{CH}$=11.0 Hz, 4.9 Hz, 2-C); IR (KBr) 3097, 3061, 2950, 2917, 2861, 1714, 1610, 1598, 1564, 1539, 1484, 1445, 1343, 1251, 1174, 1155, 1133, 1076, 1066, 1042, 1024, 995, 963, 921, 913, 892, 859, 847, 835, 787, 776, 708, 689, and 669 cm^{-1}; MS (EI) 236, 235 (M^+), 207, 180, 179, 165, 118, 116, 103, 91, 89, 77, 65, 63, 51, and 39. Found: C, 81.68; H, 5.57; N, 5.95%. Calcd for $C_{15}H_{13}NO$: C, 81.70; H, 5.56; N, 5.97%.

Dimethyl 2-(*m*-Methylbenzoyl)-5-phenylpyrrole-3,4-dicarboxylate (3b): 2.0% yield; colorless solid (from benzene–hexane); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=2.42 (3H, s, CH_3), 3.38 (3H, s, $COOCH_3$), 3.72 (3H, s, $COOCH_3$), 7.35—7.38 (2H, m, arom-H), 7.45—7.48 (3H, m, arom-H of Ph), 7.51—7.54 (2H, m, arom-H), 7.60—7.63 (2H, m, arom-H of Ph), and 9.76 (1H, brs, NH); ^{13}C NMR (67.8 MHz $CDCl_3$) δ=21.26 (CH_3), 51.79 ($COO\underline{C}H_3$), 52.08 ($COO\underline{C}H_3$), 113.48 (4-C), 124.99 (3-C), 125.51 (arom), 128.34 (arom), 128.50 (CH of Ph), 129.04 (arom), 129.11 (CH of Ph), 129.72 (4′-CH of Ph), 129.85 (2-C), 133.30 (arom), 137.75 (arom), 138.25 (arom), 140.18 (5-C), 163.66 ($\underline{C}OOCH_3$), 165.21 ($\underline{C}OOCH_3$), and 186.27 (C=O); IR (KBr) 3254 (NH), 2951, 1723, (ester-C=O), 1623 (keto-C=O), 1601, 1583, 1559, 1512, 1482, 1460, 1442, 1415, 1357, 1288, 1267, 1165, 1136, 1092, 1042, 976, 941, 852, 697, and 666 cm^{-1}.

The $Rh_2(OAc)_4$-catalyzed reaction of *p*-methyl-α-diazoacetophenone (**1c**) with benzonitrile in the presence of DMAD gave **2c** and **3c**.

5-(*p*-Methylphenyl)-2-phenyloxazole (2c): 44.6% yield; colorless crystals; mp 79.8—81.6 °C (from hexane); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=2.33 (3H, s, CH_3), 7.19 (2H, d, J=8.3 Hz, 3″-H of Ar), 7.35 (1H, s, 4-H), 7.39—7.47 (3H, m, arom-H of Ph), 7.56 (2H, d, J=8.3 Hz, 2″-H of Ar), and 8.05—8.09 (2H, m, arom-H of Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=21.21 (qt, $^3J_{CH}$=4.3 Hz, CH_3), 122.67 (d, J_{CH}=192.26 Hz, 4-CH), 124.01 (dd, $^3J_{CH}$=6.1 Hz, 3″-CH of Ar), 125.15 (m, 1″-C of Ar), 126.08 (dt, 2′-CH of Ph), 127.45 (m, 1′-C of Ph), 128.63 (dm, 2″-CH of Ar), 129.45 (dm, 3′-CH of Ph), 130.02 (dt, $^3J_{CH}$=7.6 Hz, 4′-CH of Ph), 138.29 (m, 4″-C of Ar), 151.33 (dt, $^2J_{CH}$=16.5 Hz, $^3J_{CH}$=4.6 Hz, 5-C), and 160.65 (m, 2-C); IR (KBr) 3127, 3046, 3022, 2985, 2953, 2917, 2805, 2735, 2421, 2362, 2335, 1966, 1907, 1729, 1662, 1605, 1589, 1541, 1499, 1477, 1445, 1381, 1341, 1314,

1280, 1241, 1209, 1175, 1134, 1110, 1071, 1055, 1041, 1023, 978, 952, 935, 837, 818, 793, 775, 710, 695, and 668 cm^{-1}; MS (EI) 236, 235 (M^+), 207, 180, 179, 165, 118, 104, 103, 91, 89, 77, 65, 63, and 51.

Dimethyl 2-(*p*-Methylbenzoyl)-5-phenylpyrrole-3,4-dicarboxylate (3c): 9.8% yield; colorless crystals; mp 186.4—188.2 °C (from benzene–hexane); ^1H NMR (270.05 MHz, $CDCl_3$) δ=2.41 (3H, s, CH_3), 3.39 (3H, s, $COOCH_3$), 3.71 (3H, s, $COOCH_3$), 7.23 (2H, d, J=7.9 Hz, 3″-H), 7.40—7.46 (3H, m, arom-H of Ph), 7.56—7.61 (4H, m, arom-H), and 10.53 (1H, brs, NH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=21.62 (qt, $^3J_{CH}$=4.4 Hz, CH_3), 51.68 (q, $COO\underline{C}H_3$), 51.97 (q, $COO\underline{C}H_3$), 113.54 (d, $^3J_{CH}$=7.3 Hz, 4-C), 124.68 (d, $^3J_{CH}$=6.1 Hz, 3-C), 128.31 (dm, arom-CH), 128.72 (dm, arom-CH), 128.81 (d, $^2J_{CH}$=3.1 Hz, 2-C), 128.95 (dm, arom-CH), 129.14 (dm, arom-CH), 129.44 (dt, $^3J_{CH}$=7.3 Hz, 4′-CH of Ph), 129.89 (m, 4″-C of Ar), 135.19 (t, $^2J_{CH}$=7.3 Hz, 1″-C of Ar), 140.06 (d, 5-C), 143.36 (q, 1′-C of Ph), 163.82 (m, $\underline{C}OOCH_3$), 165.08 (m, $\underline{C}OOCH_3$), and 186.40 (m, C=O); IR (KBr) 3317 (NH), 2941, 1724 (ester-C=O), 1624 (keto-C=O), 1605, 1559, 1516, 1481, 1457, 1440, 1414, 1282, 1262, 1240, 1194, 1178, 1138, 1088, 1039, 973, 923, 831, 794, 758, 698, and 669 cm^{-1}; MS (EI) 378, 377 (M^+), 346, 345, 330, 313, 314, 287, 286, 259, 173, 157, 119, 91, and 65. Found: C, 70.30; H, 5.16 ; N, 3.81%. Calcd for $C_{22}H_{19}NO_5$: C, 70.02; H, 5.07; N, 3.71%.

The $Rh_2(OAc)_4$-catalyzed reaction of α-diazoacetophenone (**1d**) with benzonitrile in the presence of DMAD gave **2d** and **3d**.

2,5-Diphenyloxazole (2d): 50.6% yield; pale yellow crystals; mp 69.1—71.2 °C (from benzene–hexane); ^1H NMR (270.05 MHz, $CDCl_3$) δ=7.31—7.38 (1H, m, arom-H), 7.42—7.53 (6H, m, arom-H and 4-H), 7.71—7.75 (2H, m, arom-H), and 8.09—8.14 (2H, m, arom-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=123.38 (d, J_{CH}=192.3 Hz, 4-CH), 124.16 (dt, 2″-CH of 5-Ph), 126.24 (dm, 2′-CH of 2-Ph), 127.38 (m, 1′-C of 2-Ph), 127.95 (m, 1″-C of 5-Ph), 128.42 (dt, 4′-CH of 2-Ph), 128.80 (dm, arom-CH), 128.90 (dm, arom-CH), 130.31 (dtd, 4″-CH of 5-Ph), 151.22 (dt, $^2J_{CH}$=17.1 Hz, $^3J_{CH}$=4.3 Hz, 5-C), and 161.10 (m, 2-C); IR (KBr) 3061, 1730, 1610, 1588, 1540, 1482, 1445, 1349, 1154, 1133, 1070, 1059, 1027, 953, 822, 775, 760, 707, and 686 cm^{-1}; MS (EI) 222, 221 (M^+), 193, 166, 165, 116, 105, 90, 89, 77, 63, 51, and 39. Found: C, 81.41; H, 5.13; N, 6.34%. Calcd for $C_{15}H_{11}NO$: C, 81.43; H, 5.01; N, 6.33%.

Dimethyl 2-Benzoyl-5-phenylpyrrole-3,4-dicarboxylate (3d): 11.0% yield; colorless crystals; mp 159.5—162.0 °C (from benzene–hexane); ^1H NMR (270.05 MHz, $CDCl_3$) δ=3.36 (3H, s, $COOCH_3$), 3.72 (3H, s, $COOCH_3$), 7.43—7.70 (10H, m, arom-H), and 10.13 (1H, brs, NH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=51.77 ($COO\underline{C}H_3$), 52.06 ($COO\underline{C}H_3$), 113.64 (4-C), 124.98 (3-C), 128.36(arom-CH), 128.50 (arom-CH), 129.06 (arom-CH), 129.70 (arom-CH), 129.79 (2-C), 137.86 (arom-C), 138.04 (5-C), 140.13(arom-C), 163.65 ($\underline{C}OOCH_3$), 165.01 ($\underline{C}OOCH_3$), and 186.34 (C=O); IR (KBr) 3631, 3311 (NH), 3055, 2991, 2951, 2860, 1728 (ester-C=O), 1624 (keto-C=O), 1596, 1573, 1558, 1513, 1482, 1464, 1444, 1408, 1360, 1319, 1290, 1268, 1231, 1195, 1153, 1135, 1093, 1041, 1020, 1001, 967, 942, 917, 817, 787, 764, 740, 698, and 662 cm^{-1}. Found: C, 69.88; H, 4.87; N, 3.66%. Calcd for $C_{21}H_{17}NO_5$: C, 69.41; H, 4.72; N, 3.85%.

The $Rh_2(OAc)_4$-catalyzed reaction of *m*-chloro-α-diazoacetophenone (**1e**) with benzonitrile in the presence of DMAD gave **2e** and **3e**.

5-(*m*-Chlorophenyl)-2-phenyloxazole (2e): 62.6% yield; colorless crystals; mp 115.1—116.1 °C (from hexane); ^1H NMR (270.05 MHz, $CDCl_3$) δ=7.29—7.33 (1H, m, 6″-H of Ar), 7.35—7.41 (1H, t, J=7.8 Hz, 5″-H of Ar), 7.48 (1H, s, 4-H), 7.48—7.52 (3H, m, arom-H of Ph), 7.58—7.62 (1H, m, 4″-H of Ar), 7.72 (1H, t, J=1.9 Hz, 2″-H of Ar), and 8.10—8.14 (2H, m, arom-H of Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=121.92 (dtd, $^2J_{CH}$=1.2 Hz, $^3J_{CH}$=6.7 Hz, 6″-CH of Ar), 123.84 (dm, 2″-CH of Ar), 124.23 (d, J_{CH}=192.9 Hz, 4-CH), 126.16 (dm, arom-CH of Ph), 126.96 (m, 1′-C of Ph), 128.05 (dm, 4″-CH of Ar), 128.61 (dm, arom-CH of Ph), 129.41 (m, 1″-C of Ar), 129.96 (d, 5″-CH of Ar), 130.31 (dt, $^3J_{CH}$=7.6 Hz, 4′-CH of Ph), 134.76 (m, 3″-C of Ar), 149.55 (dt, $^2J_{CH}$=17.1 Hz, $^3J_{CH}$=4.6 Hz, 5-C), and 161.28 (m, 2-C); IR (KBr) 3103, 1730, 1610, 1586, 1534, 1473, 1446, 1429, 1346, 1141, 1098, 1082, 960, 898, 847, 783, 763, 709, 687, 668, and 659 cm^{-1}; MS (EI) 257, 256, 255 (M^+), 227, 200, 192, 165, 128, 116, 111, 89, 77, 63, and 51. Found: C, 70.48; H, 4.05; N, 5.44%. Calcd for $C_{15}H_{10}NOCl$: C, 70.46; H, 3.94; N, 5.48%.

Dimethyl 2-(*m*-Chlorobenzoyl)-5-phenylpyrrole-3,4-dicarboxylate (3e): 15.1% yield; colorless crystals; mp 159.2—160.8 °C (from benzene–hexane); ^1H NMR (270.05 MHz, $CDCl_3$) δ=3.50 (3H, s, $COOCH_3$), 3.73 (3H, s, $COOCH_3$), 7.42 (1H, t, J=7.9 Hz, 5″-H of Ar), 7.47—7.51 (3H, m, arom-H of Ph), 7.54—7.58 (1H, m, arom-H), 7.60—7.64 (3H, m, arom-H of Ar and Ph), 7.72 (1H, m, 2″-H of Ar), and 9.62 (1H, brs, NH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=51.83 (q, $COO\underline{C}H_3$), 52.32 (q, $COO\underline{C}H_3$), 113.79 (d, $^3J_{CH}$=7.3 Hz, 4-C), 125.47 (d, $^3J_{CH}$=6.1 Hz, 3-C), 126.48 (dm, arom-CH), 127.77 (m, 1″-C of Ar), 128.42 (dm, arom-CH), 128.54 (dm, arom-CH of Ph), 129.08 (dm, arom-CH of Ph), 129.61 (m, 2-C), 129.77 (d, 5″-CH of Ar), 129.90 (dm, 4′-CH of Ph), 132.43 (dm, arom-CH), 134.48 (dm, 3″-CH of Ar), 139.27 (d, $^2J_{CH}$=8.6 Hz, 5-C), 140.71 (m, 1′-C of Ph), 163.47 (m, $\underline{C}OOCH_3$), 164.96 (m, $\underline{C}OOCH_3$), and 184.71 (m, C=O); IR (KBr) 3333 (NH), 2951, 1722 (ester-C=O), 1621 (keto-C=O), 1561, 1509, 1481, 1465, 1437, 1422, 1289, 1261, 1195, 1141, 1088, 974, 933, 819, 792, 760, and 697 cm^{-1}; MS (EI) 399, 398, 397 (M^+), 367, 366, 365, 336, 335, 334, 308, 307, 306, 279, 254, 183, 139, 111, and 75. Found: C, 63.57; H, 4.14; N, 3.62%. Calcd for $C_{21}H_{16}NO_5Cl$: C, 63.40; H, 4.05; N, 3.52%.

The $Rh_2(OAc)_4$-catalyzed reaction of *p*-chloro-α-diazoacetophenone (**1f**) with benzonitrile in the presence of DMAD gave **2f** and **3f**.

5-(*p*-Chlorophenyl)-2-phenyloxazole (2f): 63.0% yield; colorless crystals; mp 105.4—107.1 °C (from hexane); ^1H NMR (270.05 MHz, $CDCl_3$) δ=7.39 (2H, d, J=8.6 Hz, 2″-H of Ar), 7.42 (1H, s, 4-H). 7.44—7.51 (3H, m, arom-H of Ph), 7.62 (2H, d, J=8.6Hz, 3″-H of Ar), and 8.05—8.12 (2H, m, arom-H of Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=123.84 (d, J_{CH}=192.3 Hz, 4-CH), 125.42 (dd, $^3J_{CH}$=7.3 Hz, 2″-CH of Ar), 126.35 (dm, 2′-CH of Ph), 126.53 (m, arom-C), 127.27 (m, arom-C), 128.87 (dm, 3′-CH of Ph), 129.22 (dd, $^3J_{CH}$=5.5 Hz, 3″-CH of Ar), 130.51 (dt, $^3J_{CH}$=7.3 Hz, 4′-CH of Ph), 134.20 (tt, $^2J_{CH}$=11.0 Hz, $^3J_{CH}$=3.7 Hz, 4″-C of Ar), 150.28 (dt, $^2J_{CH}$=17.1 Hz, $^3J_{CH}$=4.9 Hz, 5-C), and 161.40 (m, 2-C); IR (KBr) 2927, 1730, 1631, 1541, 1482, 1449, 1405, 1340, 1274, 1134, 1092, 1062, 1055, 1012, 952,

818, 772, 705, 689, and 669 cm^{-1}; MS (EI) 255 (M^+), 227, 200, 192, 165, 239, 128, 116, 89, and 77. Found: C, 70.20; H, 4.06; N, 5.34%. Calcd for $C_{15}H_{10}NOCl$: C, 70.46; H, 3.94; N, 5.48%.

Dimethyl 2-(*p*-Chlorobenzoyl)-5-phenylpyrrole-3,4-dicarboxylate (3f): 11.0% yield; colorless crystals; mp 183.3—185.5 °C (from benzene–hexane); ^1H NMR (270.05 MHz, $CDCl_3$) δ=3.44 (3H, s, $COOCH_3$), 3.73 (3H, s, $COOCH_3$), 7.41—7.45 (2H, m, arom-H), 7.45—7.47 (3H, m, arom-H), 7.58—7.61 (2H, m, arom-H), 7.62—7.65 (2H, m, arom-H), and 10.09 (1H, brs, NH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=51.83 (q, $COO\underline{C}H_3$), 52.22 (q, $COO\underline{C}H_3$), 113.82 (d, $^3J_{CH}$=7.3 Hz, 4-C), 125.06 (d, $^3J_{CH}$=6.1 Hz, 3-C), 128.12 (d, $^2J_{CH}$=3.1 Hz, 2-C), 128.46 (dm, arom-CH of Ph), 128.63 (dd, $^3J_{CH}$=5.5 Hz, arom-CH), 129.07 (dm, arom-CH of Ph), 129.67 (dt, 4′-CH of Ph), 129.75 (m, 1″-C of Ar), 129.86 (dd, $^3J_{CH}$=6.7 Hz, arom-CH), 136.14 (t, $^2J_{CH}$=7.3 Hz, 1′-C of Ph), 138.93 (tm, $^2J_{CH}$=10.7 Hz, 4″-C of Ar), 140.46 (d, $^2J_{CH}$=3.7 Hz, 5-C), 163.59 (m, $\underline{C}OOCH_3$), 164.96 (m, $\underline{C}OOCH_3$), and 184.71 (t, $^3J_{CH}$=3.7 Hz, C=O); IR (KBr) 3327 (NH), 2949, 1725 (ester-C=O), 1621 (keto-C=O), 1587, 1566, 1513, 1483, 1462, 1442, 1415, 1356, 1288, 1263, 1242, 1134, 1094, 1040, 1015, 973, 917, 837, 791, 769, 759, 734, and 697 cm^{-1}; MS (EI) 397 (M^+), 365, 334, 306, 279, 139, and 111. Found: C, 63.28; H, 4.12; N, 3.53%. Calcd for $C_{21}H_{16}NO_5Cl$: C, 63.40; H, 4.05; N, 3.52%.

The $Rh_2(OAc)_4$-catalyzed reaction of *p*-cyano-α-diazoacetophenone (**1g**) with benzonitrile in the presence of DMAD gave **2g** and **3g**.

5-(*p*-Cyanophenyl)-2-phenyloxazole (2g): 60.9% yield; colorless crystals; mp 183.9—185.7 °C (from benzene–hexane); ^1H NMR (270.05 MHz, $CDCl_3$) δ=7.45-7.52 (3H, m, arom-H of Ph), 7.59 (1H, s, 4-H), 7.72 (2H, d, J=8.6 Hz, arom-H), 7.80 (2H, d, J=8.6 Hz, arom-H), and 8.09–8.13 (2H, m, arom-H of Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=111.49 (t, $^3J_{CH}$=8.5 Hz, 4″-C of Ar), 118.52 (t, $^3J_{CH}$=5.2 Hz, CN), 124.32 (dd, $^3J_{CH}$=6.1 Hz, 2″-CH of Ar), 126.24 (d, J_{CH}=192.9 Hz, 4-CH), 126.52 (dm, arom-CH of Ph), 126.84 (m, 1′-C of Ph), 128.92 (dm, arom-CH of Ph), 130.94 (dt, $^3J_{CH}$=7.9 Hz, 4′-CH of Ph), 131.90 (t, $^3J_{CH}$=7.9 Hz, 1″-C of Ar), 132.78 (dd, $^3J_{CH}$=6.1 Hz, 3″-CH of Ar), 149.32 (dt, $^2J_{CH}$=17.1 Hz, $^3J_{CH}$=4.3 Hz, 5-C), and 162.39 (m, 2-C); IR (KBr) 3121, 3070, 2360, 2227 (CN), 1610, 1539, 1495, 1476, 1413, 1344, 1182, 1137, 1055, 953, 839, 771, 708, 688, and 668 cm^{-1}; MS (EI) 247, 246 (M^+), 245, 218, 191, 190, 123, 116, 102, 89, 77, 63, 51, and 39. Found: C, 78.20; H, 4.25; N, 11.29%. Calcd for $C_{16}H_{10}N_2O$: C, 78.03; H, 4.09; N, 11.38%.

Dimethyl 2-(*p*-Cyanobenzoyl)-5-phenylpyrrole-3,4-dicarboxylate (3g): 9.0% yield; colorless crystals; mp 247.5—251.2 °C (from benzene–hexane); ^1H NMR (270.05 MHz, $CDCl_3$) δ=3.41 (3H, s, $COOCH_3$), 3.73 (3H, s, $COOCH_3$), 7.47—7.52 (3H, m, arom-H of Ph), 7.58—7.63 (2H, m, arom-H of Ph), 7.75—7.83 (4H, m, arom-H), and 9.63 (1H, brs, NH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=51.92 ($COO\underline{C}H_3$), 52.27 ($COO\underline{C}H_3$), 115.71 (4-C), 117.83 (C≡N), 125.58, 127.54, 128.67 (arom-CH), 128.76 (arom-CH), 128.99 (arom-CH), 129.49, 130.09 (arom-CH), 132.12 (arom-CH), 132.39, 140.90, 141.50, 163.38 ($\underline{C}OOCH_3$), 164.66 ($\underline{C}OOCH_3$), and 184.44 (C=O); IR (KBr) 3209 (NH), 2945, 2342, 2334, 2226 (CN), 1739 (ester-C=O), 1677 (keto-C=O), 1641, 1558, 1513, 1486, 1463, 1443, 1431, 1417, 1308, 1288, 1272, 1245, 1210, 1155, 1090, 1045, 961, 907, 864, 821, 797, 759, 701, and 668 cm^{-1}; MS (EI) 389, 388 (M^+), 358, 357, 356, 355, 328, 327, 326, 325, 324, 298, 297, 270, 269, 254, 242, 241, 214, 178, 138, 130, 102, and 77. Found: C, 67.75; H, 4.37; N, 6.94%. Calcd for $C_{22}H_{16}N_2O_5$: C, 68.04; H, 4.15; N, 7.21%.

The $Rh_2(OAc)_4$-catalyzed reaction of *m*-nitro-α-diazoacetophenone (**1h**) with benzonitrile in the presence of DMAD gave **2h** and **3h**.

5-(*m*-Nitrophenyl)-2-phenyloxazole (2h): 60.5% yield; colorless crystals; mp 150.3—151.8 °C (from benzene–hexane); ^1H NMR (270.05 MHz, $CDCl_3$) δ=7.49-7.54 (3H, m, arom-H of Ph), 7.61 (1H, s, 4-H), 7.64 (1H, t, J=7.9 Hz, 5″-H of Ar), 8.03 (1H, dt, J=7.9 Hz, 6″-H of Ar), 8.13—8.17 (2H, m, arom-H of Ph), 8.17—8.21 (1H, dm, 4″-H of Ar), and 8.56 (1H, t, ^3J=7.9 Hz, 2″-H of Ar); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=118.89 (dt, $^3J_{CH}$=5.5 Hz, 2″-CH of Ar), 122.78 (dm, 4″-CH of Ar), 125.53 (d, J_{CH}=192.9 Hz, 4-CH), 126.56 (dm, 2′-CH of Ph), 126.88 (m, 1′-C of Ph), 128.95 (dm, 3′-CH of Ph), 129.56 (dt, $^3J_{CH}$=7.9 Hz, 6″-CH of Ar), 129.65 (m, 1″-C of Ar), 130.08 (d, 5″-CH of Ar), 130.93 (dt, $^3J_{CH}$=7.3 Hz, 4′-CH of Ph), 148.84 (m, 3″-CH of Ar), 148.93 (m, 5-C), and 162.23 (m, 2-C); IR (KBr) 3079, 2935, 2730, 1619, 1571, 1524 (NO_2), 1476, 1448, 1349 (NO_2), 1137, 1104, 965, 902, 867, 801, 776, 738, 711, 689, and 669 cm^{-1}; MS (EI) 267, 266 (M^+), 220, 192, 165, 133, 117, 116, 105, 96, 89, 77, and 63. Found: C, 67.37; H, 3.90; N, 10.48%. Calcd for $C_{15}H_{10}N_2O_3$: C, 67.67; H, 3.79; N, 10.52%.

Dimethyl 2-(*m*-Nitrobenzoyl)-5-phenylpyrrole-3,4-dicarboxylate (3h): 12.5% yield; colorless crystals; mp 160.7—163.8 °C (from benzene–hexane); ^1H NMR (270.05 MHz, $CDCl_3$) δ=3.44 (3H, s, $COOCH_3$), 3.72 (3H, s, $COOCH_3$), 7.44—7.49 (3H, m, arom-H of Ph), 7.60—7.65 (2H, m, arom-H of Ph), 7.66 (1H, t, J=8.3 Hz, 5″-H of Ar), 7.99 (1H, d, J=7.6 Hz, 6″-H of Ar), 8.41—8.44 (dm, 4″-arom-H), 8.53 (1H, t, ^3J=1.8 Hz, 2″-H of Ar), and 10.24 (1H, brs, NH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=51.47 (q, $COO\underline{C}H_3$), 52.32 (q, $COO\underline{C}H_3$), 114.25 (d, $^3J_{CH}$=7.9 Hz, 4-C), 123.36 (dt, $^3J_{CH}$=5.2 Hz, arom-CH), 125.85 (d, $^3J_{CH}$=6.1 Hz, 3-C), 126.71 (dm, arom-CH), 127.38 (m, 1″-C of Ar), 128.51 (dm, arom-CH of Ph), 129.10 (dm, arom-CH of Ph), 129.42 (m, 2-C), 129.55 (dm, arom-CH), 129.99 (dt, $^3J_{CH}$=7.6 Hz, 4′-CH of Ph), 134.05 (dm, arom-CH), 139.07 (d, $^2J_{CH}$=7.9 Hz, 5-C), 141.29 (m, 1′-C of Ph), 147.86 (m, 3″-C of Ar), 163.36 (m, $\underline{C}OOCH_3$), 164.78 (m, $\underline{C}OOCH_3$), and 183.78 (t, $^3J_{CH}$=4.3 Hz, C=O); IR (KBr) 3277, 3245 (NH), 2952, 1724 (ester-C=O), 1626 (keto-C=O), 1558, 1530 (NO_2), 1512, 1480, 1461, 1440, 1413, 1352 (NO_2), 1303, 1289, 1257, 1233, 1202, 1135, 1125, 1108, 836, 816, 796, 774, 761, 744, 725, and 698 cm^{-1}; MS (EI) 409, 408 (M^+), 378, 377, 376, 375, 348, 347, 346, 345, 344, 318, 317, 300, 299, 298, 290, 271, 254, 244, 214, 188, 150, 140, 139, 104, and 76. Found: C, 61.83; H, 3.95; N, 6.86%. Calcd for $C_{21}H_{16}N_2O_7$: C, 61.83; H, 4.02; N, 6.79%.

The $Rh_2(OAc)_4$-catalyzed reaction of *p*-nitro-α-diazoacetophenone (**1i**) with benzonitrile in the presence of DMAD gave **2i** and **3i**.

5-(*p*-Nitrophenyl)-2-phenyloxazole (2i): 61.2% yield; yellow crystals; mp 191.6—193.3 °C (from benzene–hexane); ^1H NMR (270.05 MHz, $CDCl_3$) δ=7.51—7.55 (3H, m, arom-H of Ph), 7.66 (1H, s, 4-H), 7.87 (2H, d, J=9.2

Hz, 2″-H of Ar), 8.32 (2H, d, J=9.2 Hz, 3″-H of Ar), and 8.11—8.17 (2H, m, arom-H of Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=124.45 (dd, $^3J_{CH}$=6.7 Hz, arom-CH), 124.55 (dd, $^3J_{CH}$=4.3 Hz, arom-CH), 126.65 (dm, 2′-CH of Ph), 126.80 (m, 1′-C of Ph), 126.94 (d, J_{CH}=193.5 Hz, 4-CH), 128.98 (dm, 3′-CH of Ph), 131.11 (dt, $^3J_{CH}$=7.3 Hz, 4′-CH of Ph), 133.74 (t, $^3J_{CH}$=8.6 Hz, 1″-C of Ar), 147.12 (m, 4″-C of Ar), 149.13 (d, $^2J_{CH}$=17.1 Hz, 5-C), and 162.80 (m, 2-C); IR (KBr) 3197, 3157, 3076, 2935, 1602, 1539, 1517 (NO_2), 1473, 1448, 1378, 1334 (NO_2), 1180, 1143, 1110, 1076, 1055, 951, 934, 853, 840, 778, 752, 712, and 688 cm^{-1}; MS (EI) 267, 266 (M^+), 220, 192, 165, 133, 117, 116, 105, 96, 89, 77, and 63. Found: C, 67.87; H, 3.93; N, 10.48%. Calcd for $C_{15}H_{10}N_2O_3$: C, 67.67; H, 3.79; N, 10.52%.

Dimethyl 2-(*p*-Nitrobenzoyl)-5-phenylpyrrole-3,4-dicarboxylate (3i): 18.3% yield; yellow crystals; mp 195.6—197.9 °C (from benzene–hexane); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=3.42 (3H, s, $COOCH_3$), 3.73 (3H, s, $COOCH_3$), 7.46—7.53 (3H, m, arom-H of Ph), 7.58—7.66 (2H, m, arom-H of Ph), 7.88 (2H, d, J=8.9 Hz, 2″-H of Ar), 8.33 (2H, d, J=8.9 Hz, 3″-H of Ar), and 9.81 (1H, brs, NH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=51.92 (q, $COO\underline{C}H_3$), 52.32 (q, $COO\underline{C}H_3$), 114.30 (d, $^3J_{CH}$=7.3 Hz, 4-C), 123.48 (dd, $^3J_{CH}$=4.6 Hz, arom-CH), 125.76 (d, $^3J_{CH}$=6.1 Hz, 3-C), 127.53 (m, 1″-C of Ar), 128.64 (dm, arom-CH of Ph), 129.01 (dm, arom-CH of Ph), 129.25 (dd, $^3J_{CH}$=6.7 Hz, arom-CH), 129.45 (m, 2-C), 130.08 (dt, $^3J_{CH}$=7.3 Hz, 4′-CH of Ph), 141.09 (m, 5-C), 143.06 (t, $^2J_{CH}$=7.6 Hz, 1′-CH of Ph), 149.83 (m, 4″-CH of Ar), 163.34 (m, $\underline{C}OOCH_3$), 164.64 (m, $\underline{C}OOCH_3$), and 184.23 (m, C=O); IR (KBr) 3271 (NH), 2947, 1719 (ester-C=O), 1624 (keto-C=O), 1600, 1525 (NO_2), 1480, 1461, 1415, 1347 (NO_2), 1305, 1259, 1198, 1133, 1090, 1040, 1015, 969, 920, 853, 766, 736, and 702 cm^{-1}; MS (EI) 409, 408 (M^+), 377, 376, 330, 317, 299, 298, 290, 271, 254, 248, 214, 188, 150, 129, 104, and 76. Found: C, 61.63; H, 3.94; N, 6.64%. Calcd for $C_{21}H_{16}N_2O_7$: C, 61.77; H, 3.95; N, 6.86%.

The $Rh_2(OAc)_4$-catalyzed reaction of *o*-methyl-α-diazoacetophenone (**1j**) with benzonitrile in the presence of DMAD gave **2j**.

5-(*o*-Methylphenyl)-2-phenyloxazole (2j): 3.0% yield; colorless solid (from hexane); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=2.54 (3H, s, $-CH_3$), 7.28—7.32 (3H, m, arom-H), 7.35 (1H, s, 4-H), 7.46—7.53 (3H, m, arom-H of Ph), 7.77—7.80 (1H, m, arom-H), and 8.10—8.18 (2H, m, arom-H of Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=21.93 (qm, $-CH_3$), 126.13 (d, J_{CH}=192.9 Hz, 4-CH), 126.25 (dd, arom-CH), 126.32 (dd, 2′-CH of Ph), 126.86 (dm, arom-CH), 127.29 (m, arom-CH), 127.43 (m, arom-CH), 128.45, (dd, $^3J_{CH}$=8.6 Hz, arom-CH), 128.85 (dm, 3′-CH of Ph), 130.38 (dt, $^3J_{CH}$=7.3 Hz, 4′-CH of Ph), 131.27 (dm, 3″-CH of Ar), 134.95 (m, 2″-CH of Ar), 150.78 (dm, $^2J_{CH}$=14.0 Hz, 5-C), and 160.85 (m, 2-C); IR (KBr) 3157, 3062, 2963, 2927, 2859, 2365, 2342, 2332, 1954, 1776, 1728, 1670, 1630, 1606, 1586, 1565, 1537, 1483, 1460, 1447, 1382, 1344, 1261, 1201, 1150, 1099, 1069, 1037, 953, 936, 922, 864, 836, 802, 778, 764, 717, 709, 688, 668, and 660 cm^{-1}.

The $Rh_2(OAc)_4$-catalyzed reaction of *o*-chloro-α-diazoacetophenone (**1k**) with benzonitrile in the presence of DMAD gave **2k** and **3k**.

5-(*o*-Chlorophenyl)-2-phenyloxazole (2k): 9.0% yield; colorless crystals; mp 64.7—69.5 °C (from hexane); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=7.29 (1H, dd, J=7.6, 1.7 Hz, 6″-H of Ar), 7.39 (1H, td, J=7.6, 1.7 Hz, arom-H), 7.47—7.52 (4H, m, 3′, 4′, 5′-H of Ph and arom-H), 7.89 (1H, s, 4-H), 7.93 (1H, dd, J=7.6 Hz, 1.7 Hz, 3″-arom-H), and 8.10—8.17 (2H, m, 2′, 6′-H of Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=126.49 (dm, 2′-CH of Ph), 126.81 (m, arom-C), 127.09 (dd, $^3J_{CH}$=8.3 Hz, arom-CH), 127.17 (m, arom-C), 127.66 (dd, $^3J_{CH}$=7.9 Hz, arom-CH), 128.40 (d, J_{CH}=197.8 Hz, 4-CH), 128.87 (dd, 3′-CH of Ph), 128.96 (dd, arom-CH), 130.61 (dt, $^3J_{CH}$=7.3 Hz, 2″-CH of Ar), 130.61 (tm, $^3J_{CH}$=11.0 Hz, 2″-C of Ar), 130.78 (dd, $^3J_{CH}$=7.9 Hz, arom-CH), 147.81 (dm, $^2J_{CH}$=14.0 Hz, 5-C), and 160.99 (m, 2-C); IR (KBr) 3169, 3065, 2869, 2861, 2365, 2343, 2335, 1966, 1896, 1810, 1735, 1654, 1629, 1585, 1558, 1540, 1483, 1468, 1447, 1425, 1342, 1309, 1290, 1269, 1230, 1144, 1129, 1099, 1078, 1069, 1034, 954, 939, 920, 871, 830, 776, 763, 733, 720, 707, 688, and 668 cm^{-1}; MS (EI) 258, 257, 256 (MH^+), 228, 200, 167, 166, 165, 139, 117, 112, 89.

Dimethyl 2-(*o*-Chlorobenzoyl)-5-phenylpyrrole-3,4-dicarboxylate (3k): 1.5% yield; yellow oil; ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=3.34 (3H, s, $COOCH_3$), 3.69 (3H, s, $COOCH_3$), 7.32—7.65 (9H, m, arom-H), and 9.57 (1H, brs, NH); IR (neat) 3414 (NH), 1729 (ester-C=O), 1639 (keto-C=O), 1482, 1380, 1247, and 1097 cm^{-1}.

The $Rh_2(OAc)_4$-catalyzed reaction of ethyl diazoacetate (**7a**) in the presence of DMAD in acetonitrile gave **9a**.

Dimethyl 2-Ethoxycarbonyl-5-methylpyrrole-3,4-dicarboxylate (9a): 12.6% yield; colorless crystals; mp 163.5—164.8 °C (from benzene–hexane); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=1.34 (3H, t, J=7.3 Hz, $COOCH_2C\underline{H}_3$), 2.55 (3H, s, CH_3), 3.81 (3H, s, $COOCH_3$), 3.92 (3H, s, $COOCH_3$), 4.31 (2H, q, J=7.3 Hz, $COOC\underline{H}_2CH_3$), and 9.92 (1H, brs, NH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=13.31 (q, CH_3), 14.09 (qt, $^2J_{CH}$=2.6 Hz, $COOCH_2\underline{C}H_3$), 51.51 (q, $COO\underline{C}H_3$), 52.62 (q, $COO\underline{C}H_3$), 61.36 (tq, $^2J_{CH}$=4.3 Hz, $COO\underline{C}H_2CH_3$), 112.02 (m, 4-C), 118.18 (d, $^2J_{CH}$=2.5 Hz, 2-C), 124.22 (d, $^3J_{CH}$=6.1 Hz, 3-C), 139.11 (m, 5-C), 160.16 (m, $\underline{C}OOEt$), 163.82 (m, $\underline{C}OOCH_3$), and 166.32 (m, $\underline{C}OOCH_3$); IR (KBr) 3251 (NH), 2995, 2959, 1744 (C=O), 1714 (C=O), 1675 (C=O), 1571, 1516, 1483, 1438, 1375, 1349, 1280, 1226, 1119, 1102, 1068, 975, 954, 868, 818, 798, and 700 cm^{-1}; MS (EI) 269 (M^+), 238, 237, 192, 191, 178, 177, 165, 162, 149, 135, 107. Found: C, 53.63; H, 5.60; N, 5.11%. Calcd for $C_{12}H_{15}NO_6$: C, 53.53; H, 5.62; N, 5.20%.

The $Rh_2(OAc)_4$-catalyzed reaction of *t*-butyl diazoacetate (**7b**) in the presence of DMAD in acetonitrile gave **9b**.

Dimethyl 2-*t*-Butoxycarbonyl-5-methylpyrrole-3,4-dicarboxylate (9b): 7.4% yield; pale yellow crystals (from benzene–hexane); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=1.53 (9H, s, CH_3 of ^{t}Bu), 2.54 (3H, s, CH_3), 3.80 (3H, s, $COOCH_3$), 3.91 (3H, s, $COOCH_3$), and 9.72 (1H, brs, NH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=13.37 (q, CH_3), 28.15 (qspt, $^3J_{CH}$=4.3 Hz, CH_3 of ^{t}Bu), 51.46 (q, $COO\underline{C}H_3$), 52.52 (q, $COO\underline{C}H_3$), 82.55 (m, $^2J_{CH}$=3.7 Hz, quaternary-C of ^{t}Bu), 111.75 (m, 4-C), 119.49 (d, $^2J_{CH}$=3.1 Hz, 2-C), 123.55 (d, $^3J_{CH}$=6.7 Hz, 3-C), 138.48 (m, 5-C), 159.45 (s, $\underline{C}OO^tBu$), 163.92 (m, $\underline{C}OOCH_3$), and 166.40 (m, $\underline{C}OOCH_3$); IR (KBr) 3259 (NH), 2979, 2950, 1735 (C=O), 1708 (C=O), 1690 (C=O), 1570, 1523, 1451, 1395, 1364, 1300, 1227, 1167, 1102, 1067, 1039, 958, 900, 850, 821, 792, 771, 752, and 703 cm^{-1}; MS (EI) 297 (M^+), 241, 224, 210, 209, 192, 178, 177.

The $Rh_2(OAc)_4$-catalyzed reaction of *p*-nitrophenyl diazoacetate (**7c**) in the presence of DMAD in acetonitrile gave **9c**.

Dimethyl 5-Methyl-2-(*p*-nitrophenoxycarbonyl)-pyrrole-3,4-dicarboxylate (9c): 11.9% yield; pale yellow powder; mp 210.0—212.4 °C (from benzene); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=2.61 (3H, s, CH_3), 3.85 (3H, s, $COOCH_3$), 3.93 (3H, s, $COOCH_3$), 7.38 (2H, d, J=9.2 Hz, 2′-H of Ar), 8.30 (2H, d, J=9.2 Hz, 3′-H of Ar), and 9.29 (1H, brs, NH); IR (KBr) 3326 (NH), 3118, 3075, 3005, 2957, 2853, 1733 (C=O), 1706 (C=O), 1696 (C=O), 1612, 1588, 1568, 1522 (NO_2), 1489, 1464, 1437, 1427, 1379, 1342 (NO_2), 1301, 1268, 1234, 1209, 1166, 1154, 1107, 1053, 1009, 974, 950, 886, 866, 856, 825, 815, 792, 783, 760, 747, 709, and 685 cm^{-1}; MS (EI) 362 (M^+), 331, 224, 192, 162, 107. Found: C, 53.00; H, 3.95; N, 7.79%. Calcd for $C_{16}H_{14}N_2O_8$: C, 53.04; H, 3.90; N, 7.73%.

The $Rh_2(OAc)_4$-catalyzed reaction of ethyl diazoacetate (**7a**) in the presence of DMAD in benzonitrile gave **8d**, **9d**, and **10**.

5-Ethoxy-2-phenyloxazole (8d): 4.8% yield; colorless crystals; mp 35.0—37.9 °C (from hexane); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=1.44 (3H, t, J=6.9 Hz, CH_3), 4.16 (2H, q, J=6.9 Hz, CH_2), 6.20 (1H, s, 4-H), 7.33—7.44 (3H, m, arom-H), and 7.90—7.93 (2H, m, arom-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=14.55 (qt, $^2J_{CH}$=2.4 Hz, CH_3), 68.13 (tq, $^2J_{CH}$=4.3 Hz, CH_2), 100.80 (d, J_{CH}=196.53 Hz, 4-C), 125.31 (dm, 2′-C of Ph), 127.71 (t, $^3J_{CH}$=6.7 Hz, 1′-C of Ph), 128.69 (dm, 3′-C of Ph), 129.49 (dt, $^3J_{CH}$=7.9 Hz, 4′-C of Ph), 152.57 (dt, $^3J_{CH}$=11.0, 5.5 Hz, 2-C), and 159.83 (dt, $^2J_{CH}$=15.3 Hz, $^3J_{CH}$=2.4 Hz, 5-C); IR (KBr) 3141, 2981, 2947, 2896, 1616, 1601, 1558, 1490, 1470, 1448, 1397, 1334, 1282, 1156, 1099, 1073, 1043, 1022, 1006, 923, 890, 772, 703, and 689 cm^{-1}.

Dimethyl 2-Ethoxycarbonyl-5-phenylpyrrole-3,4-dicarboxylate (9d): 17.8% yield; colorless crystals (from benzene–hexane); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=1.29 (3H, t, J=6.9 Hz, CH_3), 3.71 (3H, s, $COOCH_3$), 3.94 (3H, s, $COOCH_3$), 4.22 (2H, q, J=6.9 Hz, CH_2), 7.39—7.47 (3H, m, arom-H), 7.49—7.63 (2H, m, arom-H), and 9.76 (1H, brs, NH); IR (KBr) 3274, 2984, 2951, 1735, 1711, 1682, 1630, 1568, 1522, 1486, 1465, 1443, 1371, 1352, 1285, 1266, 1232, 1203, 1148, 1073, 1024, 961, 863, 820, 797, 777, 760, and 699 cm^{-1}.

Dimethyl 2-Ethoxy-5-phenylfuran-3,4-dicarboxylate (10): 2.6% yield; colorless oil; ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=1.51 (3H, t, J=6.9 Hz, CH_3), 3.81 (3H, s, $COOCH_3$), 3.91 (3H, s, $COOCH_3$), 4.54 (2H, q, J=6.9 Hz, CH_2), 7.29—7.42 (3H, m, Ph), and 7.56—7.60 (2H, m, Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=14.98 (qt, $^2J_{CH}$=2.4 Hz, CH_3), 51.60 (q, $COO\underline{C}H_3$), 52.69 (q, $COO\underline{C}H_3$), 68.66 (tq, $^2J_{CH}$=4.3 Hz, CH_2), 114.75 (s, 3-C), 125.36 (dt, $^3J_{CH}$=6.7 Hz, 2′-C of Ph), 128.52 (dt, $^3J_{CH}$=7.3 Hz, 4′-C of Ph), 128.63 (t, $^3J_{CH}$=7.3 Hz, 1′-C of Ph), 128.71 (dd, $^3J_{CH}$=7.3 Hz, 3′-C of Ph), 141.98 (t, $^3J_{CH}$=4.9 Hz, 5-C), 160.56 (t, $^3J_{CH}$=3.7 Hz, 2-C), 162.36 (q, $^3J_{CH}$=4.3 Hz, $\underline{C}OOCH_3$), and 165.13 (q, $^3J_{CH}$=4.3 Hz, $\underline{C}OOCH_3$).

The $Rh_2(OAc)_4$-catalyzed reaction of *t*-butyl diazoacetate (**7b**) in the presence of DMAD in benzonitrile gave **8e** and **9e**.

5-*t*-Butoxy-2-phenyloxazole (8e): 8.7% yield; colorless oil; ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=1.44 (9H, s, CH_3 of ^{t}Bu), 6.41 (1H, s, 4-H), 7.41—7.45 (3H, m, arom-H of Ph), and 7.91—7.96 (2H, m, arom-H of Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=28.18 (qqui, $^3J_{CH}$=4.3 Hz, CH_3 of ^{t}Bu), 84.10 (m, quaternary-C of ^{t}Bu), 109.76 (d, J_{CH}=195.3 Hz, 4-CH), 125.49 (dm, 2′-CH of Ph), 127.88 (m, 1′-C of Ph), 128.69 (dm, 3′-CH of Ph), 129.67 (dt, $^3J_{CH}$=7.3 Hz, 4′-CH of Ph), 154.44 (dt, $^3J_{CH}$=4.9 Hz, 10.4 Hz, 2-C), and 156.21 (d, $^2J_{CH}$=15.3 Hz, 5-C); IR (neat) 3129, 3063, 2979, 2932, 1729, 1616, 1549, 1482, 1392, 1369, 1343, 1269, 1236, 1154, 1113, 1066, 1024, 986, 922, 850, 807, 775, 736, 708, and 690 cm^{-1}.

Dimethyl 2-*t*-Butoxycarbonyl-5-phenylpyrrole-3,4-dicarboxylate (9e): 11.2% yield; colorless crystals; mp 147.1—149.1 °C (from benzene–hexane); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=1.45 (9H, s, CH_3 of ^{t}Bu), 3.70 (3H, s, $COOCH_3$), 3.93 (3H, s, $COOCH_3$), 7.40—7.44 (3H, m, arom-H of Ph), 7.50—7.57 (2H, m, arom-H of Ph), and 9.69 (1H, brs, NH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=28.06 (qm, CH_3 of ^{t}Bu), 51.54 (q, $COO\underline{C}H_3$), 52.58 (q, $COO\underline{C}H_3$), 82.83 (m, quaternary-C of ^{t}Bu), 111.83 (d, $^3J_{CH}$=7.3 Hz, 4-C), 121.17 (d, $^2J_{CH}$=3.1 Hz, 2-C), 124.06 (d, $^3J_{CH}$=6.1 Hz, 3-C), 128.32 (dm, arom-CH of Ph), 129.34 (dm, arom-CH of Ph), 129.43 (dm, 4′-CH of Ph), 130.29 (m, 1′-C of Ph), 139.63 (m, 5-C), 159.16 (s, $\underline{C}OO^tBu$), 163.30 (m, $\underline{C}OOCH_3$), and 166.12 (m, $\underline{C}OOCH_3$); IR (KBr), 3275 (NH), 3086, 3055, 3025, 2997, 2981, 2949, 1735 (C=O), 1709 (C=O), 1687 (C=O), 1568, 1523, 1486, 1462, 1442, 1432, 1393, 1370, 1320, 1289, 1270, 1234, 1204, 1153, 1075, 1040, 1019, 999, 959, 926, 865, 847, 821, 806, 792, 763, 749, 701, 678, and 662 cm^{-1}; MS (EI) 359 (M^+), 304, 303, 285, 272, 271, 254, 240, 239, 228, 196, 195, 169. Found: C, 63.38; H, 5.91; N, 3.90%. Calcd for $C_{19}H_{21}NO_6$: C, 63.50: H, 5.89; N, 3.90%.

The $Rh_2(OAc)_4$-catalyzed reaction of *p*-nitrophenyl diazoacetate (**7c**) in the presence of DMAD in benzonitrile gave **8f** and **9f**.

5-(*p*-Nitrophenoxy)-2-phenyloxazole (8f): 28.0% yield; yellow crystals; mp 93.1—94.4 °C (from benzene–hexane); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=6.76 (1H, s, 4-H), 7.22 (2H, d, J=9.2 Hz, 2″-H of Ar), 7.43—7.48 (3H, m, H of Ph), 7.93—7.99 (2H, m, H of Ph), and 8.27 (2H, d, J=9.2 Hz, 3″-H of Ar); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=110.41 (d, J_{CH}=199.0 Hz, 4-CH), 116.68 (dd, $^3J_{CH}$=4.9 Hz, 2″-CH of Ar), 125.88 (dm, arom-CH of Ph), 126.07 (dd, $^3J_{CH}$=5.5 Hz, 3″-CH of Ar), 126.89 (m, 1′-C of Ph), 128.89 (dm, arom-CH of Ph), 130.62 (dt, $^3J_{CH}$=7.9 Hz, 4′-CH of Ph), 144.20 (m, 4″-C of Ar), 153.47 (d, $^2J_{CH}$=14.7 Hz, 5-C), 155.93 (dt, $^2J_{CH}$=11.0 Hz, $^3J_{CH}$=4.9 Hz, 2-C), and 160.90 (tt, $^2J_{CH}$=10.4 Hz, $^3J_{CH}$=3.7 Hz, 1″-C of Ar); IR (KBr) 3197, 3110, 3085, 3014, 2839, 1610, 1600, 1576, 1512 (NO_2), 1486, 1449, 1411, 1338 (NO_2), 1308, 1289, 1274, 1255, 1216, 1175, 1160, 1106, 1073, 1062, 1020, 1009, 970, 936, 922, 868, 852, 820, 791, 772, 754, 724, 705, 691, 681, 668, and 662 cm^{-1}; MS (EI) 282 (M^+) 144, 116, 105, 89, 77, 63. Found: C, 63.85; H, 3.78; N, 9.76%. Calcd for $C_{15}H_{10}N_2O_4$: C, 63.83; H, 3.57; N, 9.93%.

Dimethyl 2-(*p*-Nitrophenoxycarbonyl)-5-phenylpyrrole-3,4-dicarboxylate (9f): 13.9% yield; colorless crystals; mp 230.6—234.6 °C (from benzene–ethyl acetate); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=3.76 (3H, s, $COOCH_3$), 3.97 (3H, s, $COOCH_3$), 7.42 (2H, d, J=9.2 Hz, 2″-CH of Ar), 7.47—7.52 (3H, m, arom-CH of Ph), 7.57—7.62 (2H, m, arom-CH of Ph), 8.32 (2H, d, J=9.2 Hz, 3″-CH of Ar), and

9.35 (1H, brs, NH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=51.89 ($COO\underline{C}H_3$), 53.06 ($COOCH_3$), 112.91 (4-C), 117.92 (2-C), 122.26 (2″-CH of Ar), 125.39 (3″-CH of Ar), 126.84 (3-C), 128.59 (2′-CH of Ph), 129.19 (3′-CH of Ph), 129.52 (1′-C), 130.11 (4′-CH), 141.38 (5-C), 145.58 (4″-C of Ar), 154.59 (1″-C of Ar), 156.77 ($\underline{C}OOAr$), 162.81 ($\underline{C}OOCH_3$), and 165.48 ($\underline{C}OOCH_3$); IR (KBr) 3254 (NH), 3077, 2997, 2955, 2851, 1741 (C=O), 1714 (C=O), 1610, 1591, 1565, 1521 (NO_2), 1486, 1462, 1442, 1425, 1343 (NO_2), 1298, 1287, 1246, 1211, 1164, 1146, 1137, 1114, 1080, 1059, 1033, 1013, 956, 940, 925, 879, 864, 851, 810, 796, 767, 749, and 700 cm^{-1}; MS (EI) 425, 424 (M^+), 394, 393, 380, 361, 349, 303, 287, 286, 255, 254, 226, 224, 211, 196, 170, 169, 140, 139, 129, 127, 115, 114, 113, 105, 104, 77, 59, and 39. Found: C, 58.85; H, 3.95; N, 6.57%. Calcd for $C_{21}H_{16}N_2O_8$: C, 59.44; H, 3.80; N, 6.60%.

The $Rh_2(OAc)_4$-catalyzed reaction of ethyl diazobenzoylacetate (**11**) in benzonitrile gave **13**.

Ethyl 2,5-Diphenyloxazole-4-carboxylate (13): 6% yield; colorless solid; ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=1.43 (3H, t, J=7.3 Hz, CH_3), 4.46 (2H, q, J=7.3 Hz, CH_2), 7.47—7.54 (6H, m, arom-H), and 8.10—8.19 (4H, m, arom-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=14.30 (CH_3), 61.52 (CH_2), 121.62 (4-C), 126.36 (arom-CH), 126.88 (arom-CH), 127.11 (arom-CH), 128.41 (arom-CH), 128.57 (arom-CH), 128.80 (arom-CH), 130.31 (arom-CH), 131.09 (arom-CH), 155.11 (5-C), 159.82 (2-C), and 162.32 ($\underline{C}OOEt$); IR (KBr) 3030, 2957, 1724 (ester-C=O), 1579, 1561, 1492, 1445, 1374, 1354, 1326, 1304, 1215, 1105, 1070, 1040, 1022, 921, 841, 779, 762, 710, and 686 cm^{-1}; MS (EI) 295, 294 (MH^+), 266, 249, 222, 221, 105, 77.

The $Rh_2(OAc)_4$-catalyzed reaction of *p*-nitro-α-diazoacetophenone (**1i**) in the presence of DMAD in pentafluorobenzonitrile gave **14a**.

5-(*p*-Nitrophenyl)-2-(pentafluorophenyl)oxazole (14a): 58% yield; yellow needles; mp 170.4—171.5 °C (from benzene); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=7.79 (1H, s, 4-H), 7.89 (2H, d, J=8.9 Hz, 2′-H of Ar), and 8.35 (2H, d, J=8.9 Hz, 3′-H of Ar); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=103.45 (m, 1′-C of C_6F_5), 124.62 (dd, $^3J_{CH}$=4.3 Hz, 2″-CH of Ar), 125.05 (dd, $^3J_{CH}$=7.3 Hz, 3″-CH of Ar), 126.66 (d, J_{CH}=196.5 Hz, 4-CH), 132.66 (t, $^3J_{CH}$=7.9 Hz, 1″-C of Ar), 138.16 (dm, J_{CF}=257.6 Hz, CF of C_6F_5), 142.66 (dm, J_{CF}=260.0 Hz, CF of C_6F_5), 145.21 (dm, J_{CF}=260.6 Hz, CF of C_6F_5), 147.71 (m, 4″-C of Ar), 150.51 (dm, $^2J_{CH}$=18.3 Hz, 5-C), and 151.86 (dm, 2-C); IR (KBr) 3135, 2919, 1658, 1608, 1546, 1522 (NO_2), 1488, 1335 (NO_2), 1150, 1107, 1086, 1062, 1017, 992, 968, 946, 856, 846, 829, 754, 746, 709, and 693 cm^{-1}; MS (EI) 357, 356 (M^+), 327, 326, 310, 301, 298, 282, 270, 262, 255, 243, 206, 195, 179, 167, 150, 141, 117, 104, 89, 77, 76, 63, 51, 50, and 39. Found: C, 50.74; H, 1.59; N, 7.86%. Calcd for $C_{15}H_5F_5N_2O_3$: C, 50.58; H, 1.41; N, 7.86%.

The $Rh_2(OAc)_4$-catalyzed reaction of *p*-nitro-α-diazoacetophenone (**1i**) in the presence of DMAD in phenyl cyanate gave **14b**.

5-(*p*-Nitrophenyl)-2-(phenyloxy)oxazole (14b): 63% yield; yellow powder; mp 145.2—145.9 °C (from benzene–hexane); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=7.26—7.50 (5H, m, PhO), 7.40 (1H, s, 4-H), 7.70 (2H, d, J=8.9 Hz, 2″-H of Ar), and 8.27 (2H, d, J=8.9 Hz, 3″-H of Ar); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=119.78 (2′-CH of PhO), 123.52 (2″-CH of Ar), 124.51 (3″-CH of Ar), 124.94 (4′-CH of PhO), 126.38 (4-CH), 129.97 (3′-CH of PhO), 133.48 (1″-C of Ar), 144.94 (5-C), 146.72 (4″-C of Ar), 152.81 (1′-C of PhO), and 161.09 (2-C); IR (KBr) 3120, 3052, 1670, 1610, 1595, 1559 (NO_2), 1526, 1505, 1487, 1454, 1434, 1418, 1371, 1335 (NO_2), 1309, 1231, 1195, 1186, 1161, 1109, 1074, 1045, 1030, 1009, 994, 972, 938, 919, 847, 838, 788, 750, 735, 718, 688, and 668 cm^{-1}; MS (EI) 284, 283 (MH^+), 253, 243, 237, 193, 191, 177, 165, 150, 133, 132, 119, 105, 104, 77, 76. Found: C, 64.12; H, 3.78; N, 9.74%. Calcd for $C_{15}H_{10}N_2O_4$: C, 63.83; H, 3.57; N, 9.92%.

The $Rh_2(OAc)_4$-catalyzed reaction of *p*-nitro-α-diazoacetophenone (**1i**) in the presence of DMAD in diethylcyanamide gave **14d** and **16**.

2-Diethylamino-5-(*p*-nitrophenyl)oxazole (14d): 12% yield; orange crystals; mp 92.7—95.0 °C (from hexane); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=1.29 (6H, t, J=6.9 Hz, CH_3), 3.56 (4H, q, J=6.9 Hz, CH_2), 7.31 (1H, s, 4-H), 7.53 (2H, d, J=8.6 Hz, 2′-H of Ar), and 8.18 (2H, d, J=8.6 Hz, 3′-H of Ar); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=13.41 (CH_3), 43.05 (CH_2), 121.76 (2′-CH of Ar), 124.53 (3′-CH of Ar), 127.85 (4-CH), 134.75 (1′-C of Ar), 142.75 (5-C), 145.12 (4′-C of Ar), and 162.08 (2-C); IR (KBr) 3099, 2967, 2933, 2871, 1618 (C=N), 1603, 1591 (NO_2), 1507, 1464, 1445, 1424, 1323 (NO_2), 1222, 1188, 1152, 1107, 1084, 1031, 931, 880, 850, 788, 751, 735, 692, and 668 cm^{-1}; MS (EI) 261 (M^+), 246, 232, 218, 200, 186, 172, 149. Found: C, 59.67; H, 5.80; N, 15.87%. Calcd for $C_{13}H_{15}N_3O_3$: C, 59.76; H, 5.79; N, 16.08%.

Dimethyl (Diethylamino)ethylene-1,2-dicarboxylate (16): 0.5% yield; yellow oil; ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=1.18 (6H, t, J=7.3 Hz, CH_3), 3.18 (4H, q, J=7.3 Hz, CH_2), 3.63 (3H, s, $COOCH_3$), 3.93 (3H, s, $COOCH_3$), and 4.61 (1H, s, 2-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=12.69 (qm, CH_3), 44.89 (tm, CH_2), 50.71 (q, $COO\underline{C}H_3$), 52.87 (q, $COO\underline{C}H_3$), 82.94 (d, 2-CH), 153.82 (m, 1-C), 166.17 (m, $\underline{C}OOCH_3$), and 168.38 (m, $\underline{C}OOCH_3$); IR (neat) 2980, 2947, 1742 (C=O), 1689 (C=O), 1569 (C=C), 1448, 1425, 1378, 1360, 1296, 1224, 1198, 1160, 1129, 1078, 1047, 1011, 973, 947, 927, 863, 825, 790, 749, and 680 cm^{-1}.

The $Rh_2(OAc)_4$-catalyzed reaction of *p*-nitro-α-diazoacetophenone (**1i**) in the presence of DMAD in diisopropylcyanamide gave **14e** and **15e**.

2-Diisopropylamino-5-(*p*-nitrophenyl)oxazole (14e): 71% yield; red crystals; mp 103.9—107.6 °C (benzene–hexane); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=1.38 (12H, d, J=6.9 Hz, CH_3), 4.16 (2H, spt, J=6.9 Hz, CH of ^{i}Pr), 7.32 (1H, s, 4-H), 7.54 (2H, d, J=8.9 Hz, 2′-H of Ar), and 8.21 (2H, d, J=8.9 Hz, 3′-H of Ar); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=20.77 (qqui, $^{2,3}J_{CH}$=4.3 Hz, CH_3), 47.73 (dsxt, $^2J_{CH}$=4.3 Hz, CH of ^{i}Pr), 121.70 (dd, $^3J_{CH}$=6.7 Hz, 2′-CH of Ar), 124.64 (dd, $^3J_{CH}$=4.3 Hz, 3′-CH of Ar), 127.26 (d, J_{CH}=190.4 Hz, 4-CH), 134.86 (t, $^3J_{CH}$=7.9 Hz, 1′-C of Ar), 142.53 (dt, $^2J_{CH}$=16.5 Hz, $^3J_{CH}$=4.3 Hz, 5-C), 145.06 (m, 4′-C of Ar), and 161.90 (dt, $^2J_{CH}$=12.2 Hz, $^3J_{CH}$=6.1 Hz, 2-C); IR (KBr) 3109, 2974, 1577 (NO_2), 1500, 1468, 1403, 1382, 1367, 1327 (NO_2), 1294, 1233, 1209, 1155, 1126, 1107, 1047, 1003, 938, 914, 851, 753, 735, and 689 cm^{-1}; MS (EI) 289 (M^+), 274, 247, 246, 232, 205, 186, 159, 149. Found: C, 62.42; H, 6.58; N, 14.35%. Calcd for $C_{15}H_{19}N_3O_3$: C, 62.27; H, 6.62; N, 14.52%.

Dimethyl 2-Diisopropylamino-5-(*p*-nitrobenzoyl)-

pyrrole-3,4-dicarboxylate (15e): 8% yield; yellow crystals; mp 170.0—172.7 °C (from benzene–hexane); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=1.28 (12H, d, J=6.6 Hz, CH_3), 3.36 (3H, s, $COOCH_3$), 3.73 (3H, s, $COOCH_3$), 3.87 (2H, spt, J=6.6 Hz, CH of ^{i}Pr), 7.78 (2H, d, J=8.9 Hz, 2′-H of Ar), 8.29 (2H, d, J=8.9 Hz, 3′-H of Ar), and 8.88 (1H, brs, NH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=22.26 (qd, $^2J_{CH}$=4.3 Hz, CH_3), 22.34 (qd, $^2J_{CH}$=4.3 Hz, CH_3), 50.40 (dm, CH of ^{i}Pr), 51.57 (q, $COO\underline{C}H_3$), 52.17 (q, $COO\underline{C}H_3$), 106.45 (d, $^3J_{CH}$=6.7 Hz, 3-C), 121.63 (d, $^2J_{CH}$=3.1 Hz, 5-C), 123.28 (dd, $^3J_{CH}$=4.9 Hz, 2′-CH of Ar), 126.96 (d, $^3J_{CH}$=6.1 Hz, 4-C), 128.94 (dd, $^3J_{CH}$=7.3 Hz, 3′-CH of Ar), 143.79 (t, $^3J_{CH}$=7.9 Hz, 1′-C of Ar), 146.17 (m, 2-C), 149.28 (m, 4′-C of Ar), 163.09 (q, $^3J_{CH}$=3.7 Hz, $\underline{C}OOCH_3$), 165.36 (q, $^3J_{CH}$=2.4 Hz, $\underline{C}OOCH_3$), and 182.22 (t, $^3J_{CH}$=4.3 Hz, C=O); IR (KBr) 3453 (NH), 3198, 3106, 3071, 3032, 2962, 2875, 1731 (C=O), 1709 (C=O), 1609, 1593, 1569, 1539 (NO_2), 1517, 1457, 1439, 1405, 1369, 1344 (NO_2), 1320, 1295, 1261, 1247, 1197, 1167, 1127, 1103, 1083, 1026, 1015, 985, 962, 936, 914, 869, 847, 816, 788, 740, 717, and 670 cm^{-1}; MS (EI) 432, 431 (M^+), 430, 402, 357, 356, 342, 282, 222, 221, 208, 207, 147, 73. Found: C, 58.38; H, 5.84; N, 9.72%. Calcd for $C_{21}H_{25}N_3O_7$: C, 58.46; H, 5.84; N, 9.74%.

The $Rh_2(OAc)_4$-catalyzed reaction of *p*-nitro-α-diazoacetophenone (**1i**) in the presence of methyl propiolate in benzonitrile gave **17a** (=**2i**) and **18a**.

Methyl 2-(*p*-Nitrobenzoyl)-5-phenylpyrrole-3-carboxylate (18a): 4% yield; yellow crystals; mp 225.4—227.0 °C (from benzene); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=3.40 (3H, s, $COOCH_3$), 7.05 (1H, d, J=3.0 Hz, 4-H), 7.38—7.54 (3H, m, arom-H of Ph), 7.61—7.67 (2H, m, arom-H of Ph), 7.91 (2H, d, J=8.9 Hz, 2″-H of Ar), 8.31 (2H, d, J=8.9 Hz, 3″-H of Ar), and 9.78 (1H, brs, NH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=51.56 (q, $COO\underline{C}H_3$), 111.15 (dd, $^3J_{CH}$=7.0 Hz, 4-CH), 123.06 (m, 3-C), 123.36 (dm, 2″-CH of Ar), 125.14 (dm, 2′-CH of Ph), 129.08 (dm, 4′-CH of Ph), 129.37 (dd, arom-CH), 129.50 (dd, arom-CH), 129.68 (m, 2-C), 130.15 (m, 5-C), 137.34 (1′-C of Ph), 144.44 (t, $^3J_{CH}$=7.6 Hz, 1″-C of Ar), 149.62 (m, 4″-C of Ar), 163.94 (m, $\underline{C}OOCH_3$), and 184.99 (C=O); IR (KBr) 3293 (NH), 2949, 1728 (ester-C=O), 1618 (keto-C=O), 1597, 1513 (NO_2), 1458, 1431, 1348 (NO_2), 1298, 1275, 1259, 1204, 1098, 920, 866, 853, 774, 765, 742, 716, 689, and 668 cm^{-1}; MS (EI) 350 (M^+), 318, 272, 260, 244, 216, 196, 159, 140. Found: C, 65.34; H, 4.18; N, 7.84%. Calcd for $C_{19}H_{14}N_2O_5$: C, 65.14; H, 4.03; N, 8.00%.

The $Rh_2(OAc)_4$-catalyzed reaction of *p*-nitro-α-diazoacetophenone (**1i**) in the presence of methyl propiolate in acetonitrile gave **17b**, **18b**, and **19b**.

2-Methyl-5-(*p*-nitrophenyl)oxazole (17b): 73% yield; yellow crystals; mp 163.3—165.9 °C (from benzene–hexane); ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=2.58 (3H, s, CH_3), 7.42 (1H, s, 4-H), 7.75(2H, d, J=8.6 Hz, 2′-H of Ar), and 8.27 (2H, d, J=8.6 Hz, 3′-H of Ar); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=14.19 (q, CH_3), 124.24 (dd, $^3J_{CH}$=7.3 Hz, 2′-CH of Ar), 124.47 (dd, $^3J_{CH}$=4.9 Hz, 3′-CH of Ar), 125.46 (d, J_{CH}=193.5 Hz, 4-CH), 133.89 (t, $^3J_{CH}$=7.9 Hz, 1′-C of Ar), 146.99 (m, 4′-C of Ar), 149.13 (dt, $^2J_{CH}$=17.1 Hz, $^3J_{CH}$=4.9 Hz, 5-C), and 162.92 (qd, $^2J_{CH}$=11.6 Hz, $^3J_{CH}$=7.9 Hz, 2-C); IR (KBr) 3121, 2931, 1710, 1608 (C=N), 1555, 1505 (NO_2), 1437, 1415, 1348, 1332 (NO_2), 1281, 1218, 1134, 1107, 1061, 943, 854, 754, 690, and 669 cm^{-1}; MS (EI) 204 (M^+), 174, 158, 146, 130, 117, 103, 89. Found: C, 58.54; H, 4.04; N, 13.59%. Calcd for $C_{10}H_8N_2O_3$: 58.82; H, 3.95; N, 13.72%.

Methyl 5-Methyl-2-(*p*-nitrobenzoyl)pyrrole-3-carboxylate (18b): 4% yield; yellow crystals; ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=2.39 (3H, s, CH_3), 3.35 (3H, s, $COOCH_3$), 6.49 (1H, d, J=3.0 Hz, 4-H), 7.85 (2H, d, J=8.9 Hz, 2′-H of Ar), 8.28 (2H, d, J=8.9 Hz, 3′-H of Ar), and 9.66 (1H, brs, NH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=13.02 (qm, CH_3), 51.41 (q, $COO\underline{C}H_3$), 112.72 (dm, 4-CH), 122.62 (dd, $^2J_{CH}$=3.1 Hz, 3-C), 123.30 (dd, $^3J_{CH}$=4.3 Hz, 2′-C of Ar), 128.94 (dd, $^2J_{CH}$=3.1 Hz, 2-C), 129.47 (dd, $^3J_{CH}$=6.7 Hz, 3′-C of Ar), 134.98 (m, 5-C), 144.71 (t, $^3J_{CH}$=7.9 Hz, 1′-C of Ar), 149.53 (m, 4′-C of Ar), 164.20 (m, $\underline{C}OOCH_3$), and 184.79 (m, C=O); IR (KBr) 3277 (NH), 2949, 1725 (ester-C=O), 1617 (keto-C=O), 1595, 1515 (NO_2), 1495, 1440, 1346 (NO_2), 1316, 1283, 1240, 1201, 1092, 920, 867, 853, 838, 794, 775, 740, 720, and 669 cm^{-1}.

Methyl 5-Methyl-2-(*p*-nitrobenzoyl)pyrrole-4-carboxylate (19b): 1% yield; yellow crystals; ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=2.66 (3H, s, CH_3), 3.84 (3H, s, $COOCH_3$), 7.21 (1H, d, J=2.6 Hz, 3-H), 8.02 (2H, d, J=8.9 Hz, 2′-H of Ar), 8.36 (2H, d, J=8.9 Hz, 3′-H of Ar), and 9.72 (1H, brs, NH).

The $Rh_2(OAc)_4$-catalyzed reaction of *p*-nitro-α-diazoacetophenone (**1i**) in the presence of methyl propiolate in diisopropylcyanamide gave **17c** (=**14e**) and **18c**.

Methyl 2-Diisopropylamino-5-(*p*-nitrobenzoyl)-pyrrole-4-carboxylate (18c): 5% yield; orange crystals; ^{1}H NMR (270.05 MHz, $CDCl_3$) δ=1.33 (12H, d, J=6.9 Hz, CH_3), 3.27 (3H, s, $COOCH_3$), 3.80 (2H, spt, J=6.9 Hz, CH of ^{i}Pr), 5.92 (1H, s, 3-H), 7.76 (2H, d, J=8.9 Hz, 2′-H of Ar), 8.26 (2H, d, J=8.9 Hz, 3′-H of Ar), and 8.79 (1H, brs, NH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=20.96 (qqui, $^{2,3}J_{CH}$=4.3 Hz, CH_3), 48.32 (dm, CH of ^{i}Pr), 51.49 (q, $COO\underline{C}H_3$), 98.65 (dd, $^3J_{CH}$=4.3 Hz, 3-CH), 122.15 (d, $^3J_{CH}$=6.7 Hz, 4-C), 123.13 (dd, $^3J_{CH}$=4.3 Hz, 2′-CH of Ar), 125.83 (m, 5-C), 129.04 (dd, $^3J_{CH}$=7.3 Hz, 3′-CH of Ar), 145.23 (m, 2-C), 146.39 (t, $^3J_{CH}$=7.9 Hz, 1′-C of Ar), 148.71 (m, 4′-C of Ar), 164.85 (m, $\underline{C}OOCH_3$), and 179.86 (m, C=O); IR (KBr) 3240 (NH), 2962, 1718 (ester-C=O), 1608 (keto-C=O), 1541 (NO_2), 1520, 1467, 1341 (NO_2), 1264, 1204, 1176, 1146, 854, 834, and 668 cm^{-1}.

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