RHODIUM(II)-CATALYZED CYCLOADDITION OF CYCLIC DIAZODICARBONYL COMPOUNDS WITH NITRILES. SYNTHESIS OF TETRAHYDROBENZOXAZOLES, TETRAHYDROBENZOFURANS, AND TETRAHYDROBENZODIOXOLES

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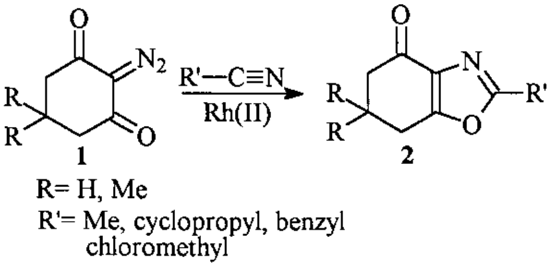
Abstract - A reaction of cyclic 2-diazodicarbonyl compounds with nitriles is described which affords tetrahydrobenzoxazoles, tetrahydrobenzofurans, and tetrahydrobenzodioxoles, depending on the structure of the nitriles.

The rhodium-catalyzed decomposition of diazocarbonyl compounds has become an important method in synthesis of heterocyclic frameworks such as furans or oxazoles.[1] In particular, the rhodium-catalyzed reaction of acyclic diazocarbonyl compounds with nitriles to give oxazoles has been reported by several groups.[2] However, the reaction of cyclic diazodicarbonyl compounds to nitriles has not been investigated. We have been interested in dipolar cycloaddition of cyclic diazodicarbonyl compounds with polar olefins such as vinyl acetates[3] and vinyl sulfides.[4] We report here our results on rhodium-catalyzed dipolar cycloaddition of cyclic diazodicarbonyl compounds with nitriles to afford tetrahydrobenzoxazoles, tetrahydrobenzofurans, and tetrahydrobenzodioxoles.

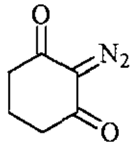
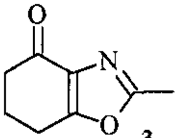
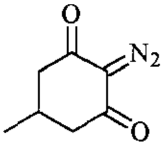
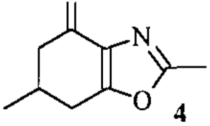
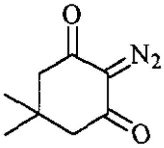
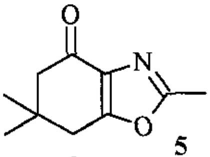
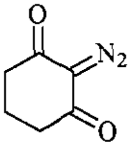
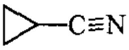
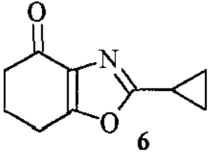
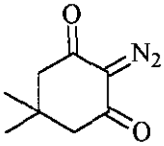
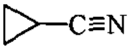
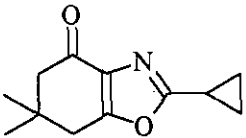
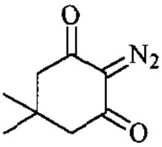
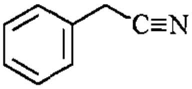
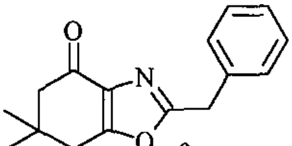
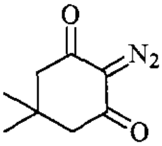
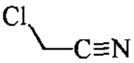
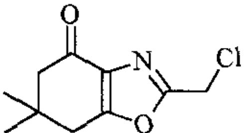
The reactions are conducted at 60 °C in the presence of 2 mol % of $Rh_2(OAc)_4$ and nitriles which serve as the solvent and reagent. Treatment of 2-diazo cyclohexane-1,3-diones (**1**) with nitriles gave tetrahydrobenzoxazoles (**2**) in moderate yields (Scheme 1). The structure of obtained tetrahydrobenzoxazoles is easily established spectroscopically. In particular, in the IR spectrum the tetrahydrobenzoxazoles are identified by the imine absorption peak of the oxazole ring at ~1685 cm^{-1}. The results are collected in Table 1. In each case, only a single product was seen and no regioisomers were found.



Scheme 1

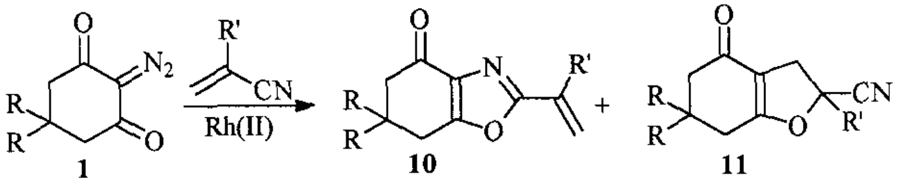
Next, the reactions of cyclic diazodicarbonyl compounds with vinylic nitriles and allyl cyanide were investigated. Reaction of cyclic 2-diazo-1,3-dicarbonyl compounds (**1**) with acrylonitriles gave tetrahydrobenzoxazoles (**10**) and the unexpected tetrahydrobenzofurans (**11**) as a mixture of regioisomers (Scheme 2). The structure of the two isomers was assigned on the basis of the NMR and IR spectra. In the ^1H NMR spectrum of tetrahydrobenzoxazole (**12**), three signals of vinylic protons were found at δ 6.53 (1H, dd, J = 17.7, 11.2 Hz), 6.21 (1H, d, J = 17.6 Hz), and 5.66 (1H, d, J = 11.2 Hz) with 1:1:1 integration ratios. On the other hand, the methine proton of tetrahydrobenzofuran (**13**) was observed at

Table 1. Synthesis of tetrahydrobenzoxazoles

entry	2-diazo-1,3-dicarbonyl compound	nitrile	product	yield (%)
1		Me—C≡N	 **3**	65
2		Me—C≡N	 **4**	65
3		Me—C≡N	 **5**	68
4			 **6**	45
5			 **7**	55
6			 **8**	42
7			 **9**	45

δ 5.28 as double doublets, and the IR spectrum exhibited a nitrile absorption at 2249 cm^{-1}. The results are collected in Table 2. Entries 1-2 using acrylonitrile resulted in the formation of a predominance of the tetrahydrobenzoxazoles rather than the dihydrofuran formation. In the use of methacrylonitrile (entries 3-5) as a reagent, the ratio of the tetrahydrofurans to tetrahydrobenzoxazoles has somewhat increased. However, when the reaction was carried out with allyl cyanide, the tetrahydrofurans were isolated as the major component.

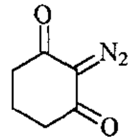
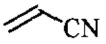
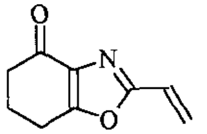
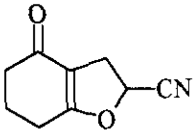
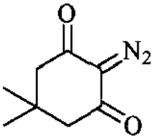
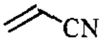
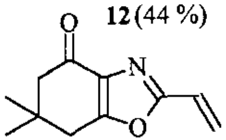
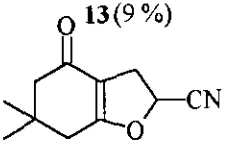
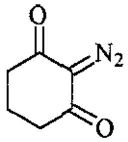
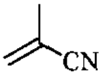
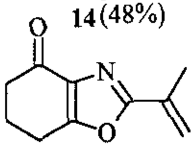
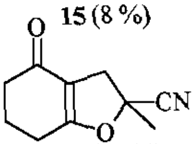
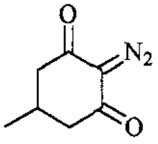
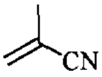
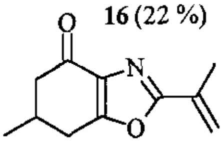
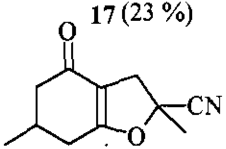
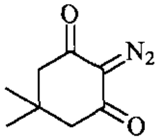
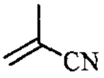
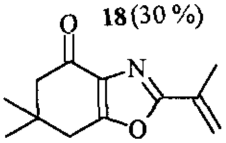
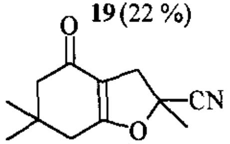
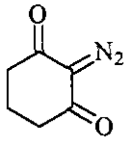
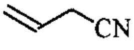
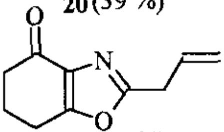
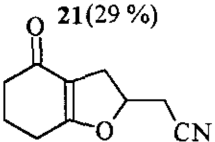
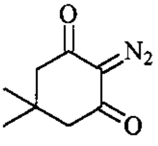
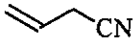
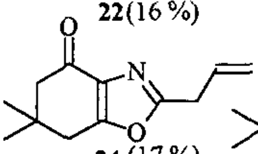
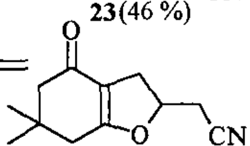
Although the exact mechanism of the reaction is still not clear, it is best described as shown in Scheme 3. While the formation of tetrahydrobenzoxazoles (**10**) may involves the 1,3-dipolar cycloaddition of carbonylcarbene (or metal carbenoid) to the nitrile (path a) or initial formation of a nitrile ylide and



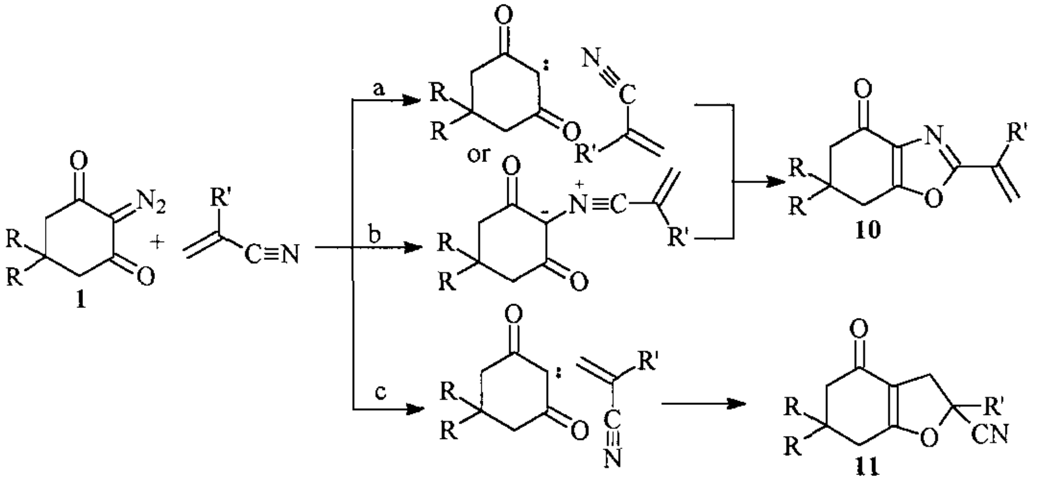
R=H, Me
R'=H, Me

Scheme 2

Table 2. Synthesis of tetrahydrobenzoxazoles and tetrahydrobenzofurans

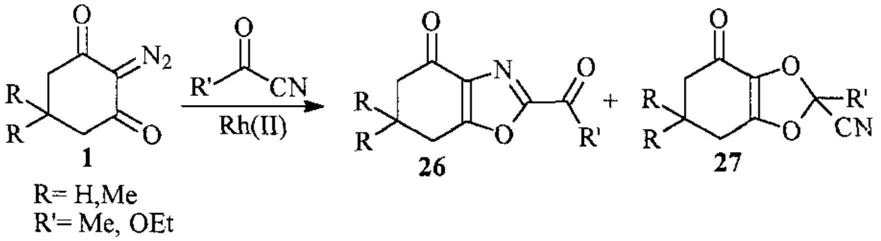
entry	2-diazo-1,3-dicarbonyl compound	nitrile	product (yield)	
1			 **12** (44 %)	 **13** (9 %)
2			 **14** (48%)	 **15** (8 %)
3			 **16** (22 %)	 **17** (23 %)
4			 **18** (30 %)	 **19** (22 %)
5			 **20** (39 %)	 **21** (29 %)
6			 **22** (16 %)	 **23** (46 %)
7			 **24** (17 %)	 **25** (45 %)

cyclization (path b), the formation of tetrahydrobenzofurans (**11**) probably seems to proceed *via* 1,3-dipolar cycloaddition (path c).[5]



Scheme 3

Finally, reaction of cyclic 2-diazo-1,3-dicarbonyl compounds with 2-oxonitriles was also examined (Scheme 4). The reaction of cyclic diazodicarbonyl compounds (**1**) with 2-oxonitriles gave tetrahydrobenzoxazoles (**26**) and unexpected tetrahydrobenzodioxoles (**27**) as a mixture of regioisomers. The structure of the two isomers was also confirmed by ^{1}H NMR and IR. The results are also summarized in Table 3.

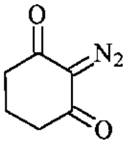
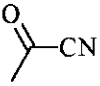
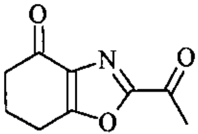
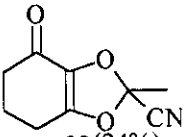
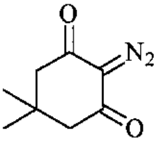
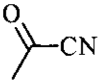
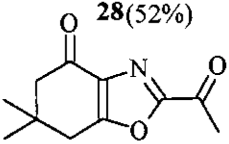
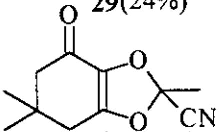
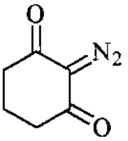
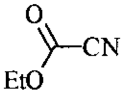
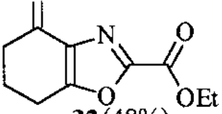
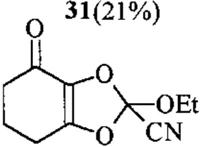
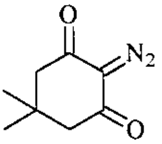
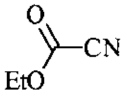
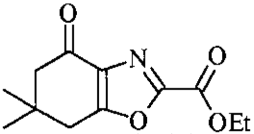
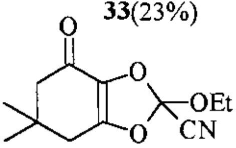


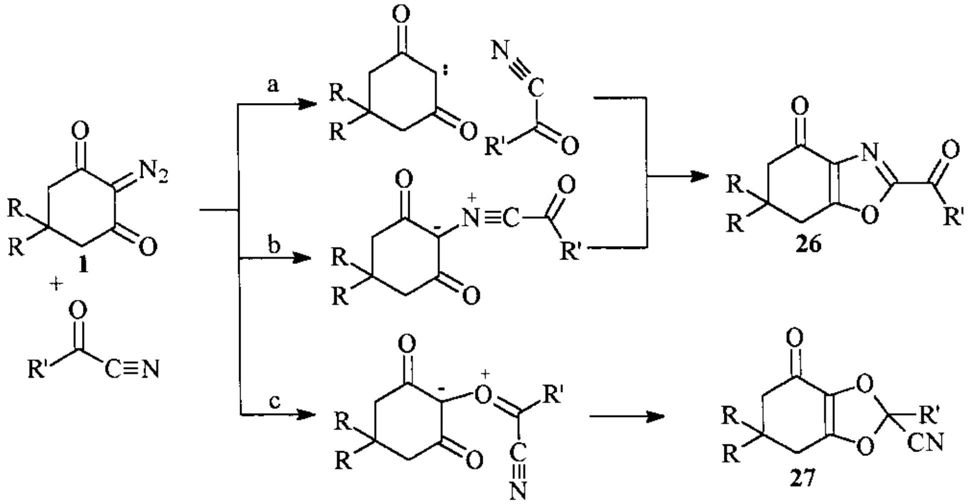
Scheme 4

The mechanistic pathways for this reaction may also be described in Scheme 5. The formation of tetrahydrobenzoxazoles (**26**) may involve the 1,3-dipolar cycloaddition of carbonylcarbene (or metal carbenoid) to the nitrile (path a) or formation of a nitrile ylide and cyclization (path b). The formation of tetrahydrobenzodioxoles (**27**) is likely to proceed *via* carbonyl ylide formation (path c).[5]

In conclusion, rhodium-catalyzed reaction of cyclic 2-diazodicarbonyl compounds with nitriles is described.

Table 3. Synthesis of tetrahydrobenzoxazoles and tetrahydrobenzodioxoles.

entry	2-diazo-1,3-dicarbonyl compound	nitrile	product (%)	
1			 **28**(52%)	 **29**(24%)
2			 **30**(46%)	 **31**(21%)
3			 **32**(48%)	 **33**(23%)
4			 **34**(40%)	 **35** (42%)



Scheme 5

EXPERIMENTAL

All experiments were carried out under a nitrogen atmosphere. Merck precoated silica gel plates (Art. 5554) with fluorescent indicator were used for analytical TLC. Flash column chromatography was performed using silica gel 9385 (Merck). Melting points were determined in capillary tubes on a Fisher-

Johns apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker Model ARX (300 MHz) spectrometer. IR spectra were recorded on a JASCO FTIR 5300 spectrophotometer. Combustion analyses were carried out at Scientific Instrument Center, Yeungnam University, Korea.

2-Methyl-4,5,6,7-tetrahydrobenzoxazol-4-one (3)

To a solution of 2-diazocyclohexane-1,3-dione (276 mg, 2.0 mmol) in acetonitrile (3 mL) was added rhodium acetate (17.7 mg, 0.04 mmol) at rt and the mixture was heated under nitrogen for 5 h at 60 °C. Evaporation and purification by silica gel chromatography with 33 % ethyl acetate in hexane as an eluent afforded the tetrahydrobenzoxazole (**3**) (197 mg, 65 %) as a liquid: ^{1}H NMR δ 2.86 (2H, t, J= 6.2 Hz), 2.49 (2H, t, J= 6.5 Hz), 2.42 (3H, s), 2.15 (2H, m); IR (neat) 2995, 1690, 1613, 1593, 1399, 1209, 1059, 1017, 893 cm $^{-1}$.

2,6-Dimethyl-4,5,6,7-tetrahydrobenzoxazol-4-one (4)

Reaction of 2-diazo-5-methylcyclohexane-1,3-dione (170 mg, 1.12 mmol) with acetonitrile (3 mL) using rhodium acetate (9.9 mg, 0.02 mmol) as a catalyst afforded **4** (120 mg, 65 %) as a liquid: ^{1}H NMR δ 3.08 (1H, dd, J=16.6, 4.5 Hz), 2.73-2.62 (3H, m), 2.57 (3H, s), 2.40 (1H, dd, J=15.7, 11.3 Hz), 1.28 (3H, d, J= 6.3 Hz); IR (neat) 2961, 1690, 1615, 1399, 1204, 1055, 1040 cm $^{-1}$; EIMS m/z (rel intens) 165(M^+, 42), 123 (100), 95 (24), 81 (5); HRMS m/z (M^+) for $C_9H_{11}NO_2$, calcd 165.0790. found 165.0779.

2,6,6-Trimethyl-4,5,6,7-tetrahydrobenzoxazol-4-one (5)

Reaction of 2-diazo-5,5-dimethylcyclohexane-1,3-dione (170 mg, 1.02 mmol) with acetonitrile (3 mL) using rhodium acetate (9.1 mg, 0:02 mmol) as a catalyst afforded **5** (125 mg, 68 %) as a solid: mp 70-71 °C; ^{1}H NMR δ 2.94 (2H, s), 2.65 (3H, s), 2.59 (2H, s), 1.32 (6H, s); IR (KBr) 2961, 1690, 1617, 1593, 1399, 1207, 1049 cm $^{-1}$.

2-Cyclopropyl-4,5,6,7-tetrahydrobenzoxazol-4-one (6)

Reaction of 2-diazo cyclohexane-1,3-dione (150 mg, 1.09 mmol) with cyclopropyl cyanide (3 mL) using rhodium acetate (9.6 mg, 0.02 mmol) as a catalyst afforded **6** (87 mg, 45 %) as a solid: mp 105-107 °C; ^{1}H NMR δ 2.90 (2H, t, J= 6.3 Hz), 2.54 (2H, t, J= 6.0 Hz), 2.20 (2H, m), 2.04 (1H, m), 1.14 (2H, m), 1.07 (2H, m); IR (neat) 2949, 1678, 1614, 1583, 1404, 1379, 1194, 1171, 1082, 1057, 1020 cm $^{-1}$; Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.25; N, 7.91. Found: C, 67.92; H, 6.33; N, 7.78.

2-Cyclopropyl-6,6-dimethyl-4,5,6,7-tetrahydrobenzoxazol-4-one (7)

Reaction of 2-diazo-5,5-dimethylcyclohexane-1,3-dione (150 mg, 0.90 mmol) with cyclopropyl cyanide (3 mL) using rhodium acetate (8.0 mg, 0.02 mmol) as a catalyst afforded 7 (96 mg, 55 %) as a liquid: ^{1}H NMR δ 2.75 (2H, s), 2.41 (2H, s), 2.02 (1H, m), 1.14 (6H, s), 1.13-1.01 (4H, m); IR (neat) 2961, 1690, 1616, 1589, 1508, 1468, 1402, 1372, 1217, 1182, 1047, 974 cm $^{-1}$; EIMS m/z (rel intens) 205 (M^+, 100), 190 (10), 178 (6), 159 (12), 149 (40), 121 (26), 83 (10), 69 (38); HRMS m/z (M^+) for $C_{12}H_{15}NO_2$, calcd 205.1103. found 205.1103.

2-Benzyl-6,6-dimethyl-4,5,6,7-tetrahydrobenzoxazol-4-one (8)

Reaction of 2-diazo-5,5-dimethylcyclohexane-1,3-dione (200 mg, 1.20 mmol) with benzyl cyanide (3 mL) using rhodium acetate (10.6 mg, 0.04 mmol) as a catalyst afforded **8** (123 mg, 42 %) as a liquid: ^{1}H NMR δ 7.29 (5H, m), 4.12 (2H, s), 2.75 (2H, s), 2.42 (2H, s), 1.46 (6H, s); IR (neat) 2961, 1694, 1582, 1399, 1179, 1049, 729 cm $^{-1}$; EIMS m/z (rel intens) 255 (M^+, 100), 240 (14), 199 (69), 123 (9), 105 (18), 91 (87); HRMS m/z (M^+) for $C_{16}H_{17}NO_2$, calcd 255.1259. found 255.1261.

2-Chloromethyl-6,6-dimethyl-4,5,6,7-tetrahydrobenzoxazol-4-one (9)

Reaction of 2-diazo-5,5-dimethylcyclohexane-1,3-dione (200 mg, 1.20 mmol) with chloroacetonitrile (3 mL) using rhodium acetate (10.6 mg, 0.04 mmol) as a catalyst afforded **9** (116 mg, 45 %) as a solid: mp

46-48 °C; ^{1}H NMR δ 4.60 (2H, s), 2.83 (2H, s), 2.45 (2H, s), 1.16 (6H, s); IR (KBr) 2969, 1676, 1399, 1051, 804, 723 cm $^{-1}$; EIMS m/z (rel intens) 213 (M$^+$, 100), 198 (76), 178 (46), 157 (8), 69 (8); HRMS m/z (M$^+$) for $C_{10}H_{12}NO_2Cl$, calcd 213.0557. found 213.0555; Anal. Calcd for $C_{10}H_{12}NO_2Cl$: C, 56.22; H, 5.66; N, 6.56. Found: C, 56.04; H, 5.69; N, 6.57.

2-Vinyl-4,5,6,7-tetrahydrobenzoxazol-4-one (12) and 2-cyano-4,5,6,7-tetrahydrobenzofuran-4-one (13)

Reaction of 2-diazocyclohexane-1,3-dione (145 mg, 1.05 mmol) with acrylonitrile (3 mL) using rhodium acetate (9.3 mg, 0.02 mmol) as a catalyst afforded **12** and **13** (91 mg, 53 %) as a mixture of 83 : 17. **12:** (44 %) ^{1}H NMR δ 6.53 (1H, dd, J= 17.7, 11.2 Hz), 6.21 (1H, d, J= 17.6 Hz), 5.66 (1H, d, J= 11.2 Hz), 2.92 (2H, t, J= 6.2 Hz), 2.53 (2H, t, J= 6.7 Hz), 2.16 (2H, m). **13:** (9 %) ^{1}H NMR δ 5.28 (1H, dd, J= 10.7, 6.7 Hz), 3.14 (2H, m), 2.74-2.09 (5H, m).

2-Vinyl-6,6-dimethyl-4,5,6,7-tetrahydrobenzoxazol-4-one (14) and 2-cyano-6,6-dimethyl-4,5,6,7-tetrahydrobenzofuran-4-one (15)

Reaction of 2-diazo-5,5-dimethylcyclohexane-1,3-dione (166 mg, 1.0 mmol) with acrylonitrile (3 mL) using rhodium acetate (8.9 mg, 0.02 mmol) as a catalyst afforded **14** and **15** (107 mg, 56 %) as a mixture of 86 : 14. **14:** (48 %) ^{1}H NMR δ 6.69 (1H, dd, J= 17.6, 11.2 Hz), 6.37 (1H, d, J= 17.6 Hz), 5.82 (1H, d, J= 11.2 Hz), 2.94 (2H, s), 2.57 (2H, s), 1.28 (3H, s) ; EIMS m/z (rel intens) 191 (M$^+$, 40), 176 (13), 135 (100), 107 (15), 83 (16), 69 (43); **15:** (8 %) ^{1}H NMR δ 5.47 (1H, dd, J= 10.7, 6.6 Hz), 3.29 (2H, m), 2.45 (2H, m), 2.36 (2H, d, J= 5.0 Hz), 1.23 (3H, s), 1.20 (3H, s) HRMS m/z (M$^+$) for $C_{11}H_{13}NO_2$, calcd 191.0946. found 191.0946.

2-Isopropenyl-4,5,6,7-tetrahydrobenzoxazol-4-one (16) and 2-cyano-2-methyl-4,5,6,7-tetrahydrobenzofuran-4-one (17)

Reaction of 2-diazo cyclohexane-1,3-dione (138 mg, 1.0 mmol) with methacrylonitrile (3 mL) using rhodium acetate (8.9 mg, 0.02 mmol) as a catalyst afforded **16** (39 mg, 22 %) and **17** (41 mg, 23 %) as a mixture. **16:** mp 110-112℃; ^{1}H NMR δ 5.95 (1H, s), 5.41 (1H, s), 2.91(2H, t, J= 6.1 Hz), 2.53 (2H, t, J= 6.5 Hz), 2.18 (2H, m), 2.12 (3H, s); IR (KBr) 2959, 1681, 1544, 1399, 1168, 1064, 1017, 921, 898 cm $^{-1}$; EIMS m/z (rel intens) 177 (M$^+$, 100), 149 (65), 136 (5), 121 (32), 108 (3), 79 (3), 69 (30); HRMS m/z (M$^+$) for $C_{10}H_{11}NO_2$, calcd 177.0790. found 177.0787; Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.25; N, 7.91. Found: C, 67.70; H, 6.31; N, 7.92. **17:** mp 55-57℃; ^{1}H NMR δ 3.26 (1H, d, J= 15.0 Hz), 2.86 (1H, d, J=15.0 Hz), 2.40 (2H, m), 2.31 (2H, m), 2.04 (2H, m), 1.76 (3H, s); IR (KBr) 2952, 2241, 1648, 1399, 1239, 1182, 1001, 900, 855 cm $^{-1}$; EIMS m/z (rel intens) 177 (M$^+$, 55), 149 (100), 126 (34), 98 (27), 70 (34); HRMS m/z (M$^+$) for $C_{10}H_{11}NO_2$, calcd 177.0790. found 177.0783; Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.25; N, 7.91. Found: C, 67.45; H, 6.36; N, 8.01.

2-Isopropenyl-6-methyl-4,5,6,7-tetrahydrobenzoxazol-4-one (18) and 2-cyano-2,6-dimethyl-4,5,6,7-tetrahydrobenzofuran-4-one (19)

Reaction of 2-diazo-5-methylcyclohexane-1,3-dione (152 mg, 1.0 mmol) with methacrylonitrile (3 mL) using rhodium acetate (8.9 mg, 0.02 mmol) as a catalyst afforded **18** (57 mg, 30 %) and **19** (42 mg, 22 %) as a mixture. **18:** mp 58-61℃; ^{1}H NMR δ 5.94 (1H, s), 5.40 (1H, s), 2.97 (1H, dd, J= 17.0, 4.5 Hz), 2.63-2.22 (5H, m), 2.11 (3H, s), 1.14 (3H, d, J= 6.3 Hz); IR(KBr) 2961, 1695, 1648, 1545, 1399, 1379, 1169, 1055, 1038, 914 cm $^{-1}$. **19:** mp 56-58℃; ^{1}H NMR δ 3.36 (1H, dd, J= 15.0, 2.6 Hz), 2.53-2.09 (5H, m), 1.85 and 1.82 (3H, s, two diastereomers), 1.16 and 1.14 (3H, d, two diastereomers) ; IR (KBr) 2960, 1652, 1399, 1219, 1021, 918, 881 cm $^{-1}$.

2-Isopropenyl-6,6-dimethyl-4,5,6,7-tetrahydrobenzoxazol-4-one (20) and 2-cyano-2,6,6-trimethyl-4,5,6,7-tetrahydrobenzofuran-4-one (21)

Reaction of 2-diazo-5,5-dimethylcyclohexane-1,3-dione (166 mg, 1.0 mmol) with methacrylonitrile (2 mL) using rhodium acetate (8.9 mg, 0.02 mmol) as a catalyst afforded **20** (80 mg, 39 %) and **21** (60 mg, 29 %) as a mixture. **20:** mp 87-89℃; ^{1}H NMR δ 6.02 (1H, s), 5.49 (1H, s), 2.85 (2H, s), 2.49 (2H, s), 2.21(3H, s), 1.20 (6H, s); IR (KBr) 2961, 1694, 1400, 1341, 1221, 1184, 1049, 918 cm^{-1}; EIMS m/z (rel intens) 205 (M^+, 56), 190 (14), 166 (67), 149 (100), 110 (16), 93 (17), 83 (45); HRMS m/z (M^+) for $C_{12}H_{15}NO_2$, calcd 205.1103. found 205.1100. **21:** mp 75-78℃; ^{1}H NMR δ 3.28 (1H, d, J= 15.0 Hz), 2.87 (1H, d, J= 15.0 Hz), 2.35-2.19 (4H, m), 1.76 (3H, s), 1.08 (3H, s), 1.04 (3H, s); IR(KBr) 2965, 1644, 1397, 1348, 1271, 1230, 1030, 885 cm^{-1}; EIMS m/z (rel intens) 205 (M^+, 28), 190 (8), 149 (100), 110 (3), 93 (7), 80 (5), 69 (5); HRMS m/z (M^+) for $C_{12}H_{15}NO_2$, calcd 205.1103. found 205.1108.

2-Allyl-4,5,6,7-tetrahydrobenzoxazol-4-one (22) and 2-cyanomethyl-4,5,6,7-tetrahydrobenzofuran-4-one (23)

Reaction of 2-diazo cyclohexane-1,3-dione (150 mg, 1.09 mmol) with allyl cyanide (3 mL) using rhodium acetate (8.9 mg, 0.02 mmol) as a catalyst afforded **22** (31 mg, 16 %) and **23** (89 mg, 46 %). **22:** ^{1}H NMR δ 5.98 (1H, m), 5.25 (1H, d, J= 17.0 Hz), 5.21 (1H, d, J= 10.0 Hz), 3.56 (2H, d, J= 6.7 Hz), 2.93 (2H, t, J= 6.2 Hz), 2.56 (2H, t, J= 6.1 Hz), 2.19 (2H, m); IR (neat) 2957, 1690, 1610, 1584, 1397, 1181, 1059, 1016, 930 cm^{-1}. **23:** ^{1}H NMR δ 5.02 (1H, m), 3.08 (1H, m), 2.73 (3H, m), 2.47 (2H, m), 2.37 (2H, t, J= 6.9 Hz), 2.06 (2H, m); IR(neat) 2955, 2253, 1635, 1406, 1233, 1182, 1140, 1113, 1063, 972 cm^{-1}.

2-Allyl-6,6-dimethyl-4,5,6,7-tetrahydrobenzoxazol-4-one (24) and 2-cyanomethyl-6,6-dimethyl-4,5,6,7-tetrahydrobenzofuran-4-one (25)

Reaction of 2-diazo-5,5-dimethylcyclohexane-1,3-dione (200 mg, 1.20 mmol) with allyl cyanide (3 mL) using rhodium acetate (10.7 mg, 0.02 mmol) as a catalyst afforded **24** (42 mg, 17 %) and **25** (111 mg, 45 %) as a mixture. **24:** mp 48-51℃; ^{1}H NMR δ δ 5.96 (1H, m), 5.21 (1H, d, J= 17.0 Hz), 5.18 (1H, d, J= 9.9 Hz), 3.52 (2H,d, J= 6.7 Hz), 2.75 (2H, s), 2.39 (2H, s), 1.13 (6H, s); IR (KBr) 2961, 1694, 1583, 1399, 1183, 1049 cm^{-1}; Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.36; N, 6.82. Found: C, 69.90; H, 7.44; N, 7.14. **25:** mp 82-84; ^{1}H NMR δ 5.00 (1H, m), 3.07 (1H, dd, J= 14.8, 10.1 Hz), 2.82-2.60 (3H, m), 2.30 (2H, s), 2.28 (2H, s), 1.10 (3H, s), 1.08 (3H, s); IR(KBr) 2969, 2251, 1615, 1418, 1366, 1221, 981, 826 cm^{-1}; EIMS m/z (rel intens) 205 (M^+, 41), 190 (10), 179 (21), 163 (27), 149 (73), 83 (100); HRMS m/z (M^+) for $C_{12}H_{15}NO_2$, calcd 205.1103. found 205.1105; Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.36; N, 6.82. Found: C, 70.53; H, 7.47; N, 6.86.

2-Acetyl-4,5,6,7-tetrahydrobenzoxazol-4-one (28) and 2-cyano-2-methyl-4,5,6,7-tetrahydrobenzodioxol-4-one (29)

Reaction of 2-diazo cyclohexane-1,3-dione (138 mg, 1.0 mmol) with pyruvonitrile (3 mL) using rhodium acetate (8.9 mg, 0.02 mmol) as a catalyst afforded **28** (93 mg, 52 %) and **29** (43 mg, 24 %) as a mixture. **28:** mp 86-87℃; ^{1}H NMR δ 3.05 (2H, t, J= 6.2 Hz), 2.69 (3H, s), 2.64 (2H, t, J= 6.4 Hz), 2.27 (2H, m); IR (KBr) 2939, 1699, 1528, 1400, 1352, 1110, 1017, 899 cm^{-1}. **29:** ^{1}H NMR δ 2.73-2.44 (4H, m), 2.13 (2H, m), 2.08 (3H, s); IR (neat) 2955, 2241, 1680, 1366, 1252, 1163, 1078, 1011, 912, 849 cm^{-1}.

2-Acetyl-6,6-dimethyl-4,5,6,7-tetrahydrobenzoxazol-4-one (30) and 2-cyano-2,6,6-trimethyl-4,5,6,7-tetrahydrobenzodioxol-4-one (31)

Reaction of 2-diazo-5,5-dimethylcyclohexane-1,3-dione (200 mg, 1.2 mmol) with pyruvonitrile (3 mL) using rhodium acetate (10.5 mg, 0.02 mmol) as a catalyst afforded **30** (115 mg, 46 %) and **31** (52 mg, 21 %) as a mixture. **30:** mp 103-105℃; ^{1}H NMR δ 2.62-2.03 (4H, m), 2.09 (3H, s), 1.21(3H, s), 1.15 (3H, s); IR (KBr) 2965, 1705, 1528, 1470, 1397, 1345, 1273, 1211, 1132, 1098, 964 cm^{-1}; EIMS m/z (rel intens) 207 (M^+, 100), 192 (30), 164 (9), 151 (50), 123 (14), 109 (58), 83 (21); HRMS m/z (M^+) for $C_{11}H_{13}NO_3$, calcd 207.0895. found 207.0894; Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76.

Found: C, 63.42; H, 6.40; N, 6.84. **31:** ^{1}H NMR δ 2.91 (2H, s), 2.70 (3H, s), 2.53 (2H, s), 1.19 (6H, s); IR (neat) 2965, 2242, 1768, 1678, 1373, 1352, 1182, 1071, 909 cm $^{-1}$; EIMS m/z (rel intens) 207 (M$^+$, 48), 190 (15), 180 (10), 169 (77), 151 (100), 133 (13), 123 (22), 110(7), 99 (13), 79 (15), 69 (5); HRMS m/z (M$^+$) for $C_{11}H_{13}NO_3$, calcd 207.0895. found 207.0898; Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76. Found: C, 63.73; H, 6.54; N, 6.80.

2-Ethoxycarbonyl-4,5,6,7-tetrahydrobenzoxazol-4-one (32) and 2-cyano-2-ethoxy-4,5,6,7-tetrahydrobenzodioxol-4-one (33)

Reaction of 2-diazo cyclohexane-1,3-dione (150 mg, 1.09 mmol) with ethyl cyanoformate (3 mL) using rhodium acetate (8.9 mg, 0.02 mmol) as a catalyst afforded **32** (109 mg, 48 %) and **33** (52 mg, 23 %) as a mixture. **32:** mp 84-86℃; ^{1}H NMR δ 4.47 (2H, q, J= 7.1 Hz), 3.07 (2H, t, J= 6.3 Hz), 2.65 (2H, t, J= 6.5 Hz), 2.29 (2H, m), 1.43 (3H, t, J= 7.1Hz); IR(KBr) 2961, 1742, 1692, 1549, 1399, 1321, 1223, 1169, 1140, 1015, 899 cm $^{-1}$; EIMS m/z (rel intens) 209 (M$^+$, 75), 181 (14), 164 (20), 137 (53), 109 (100), 81 (10); HRMS m/z (M$^+$) for $C_{10}H_{11}NO_4$, calcd 209.0688. found 209.0687; Anal. Calcd for $C_{10}H_{11}NO_4$: C, 57.42; H, 5.30; N, 6.70. Found: C, 57.72; H, 5.41; N, 6.61. **33:** mp 52-54℃; ^{1}H NMR δ 3.89 (2H, m), 2.67 (2H, m), 2.49 (2H, m), 2.16 (2H, m), 1.33 (3H, t, J= 7.1Hz); IR (KBr) 2953, 2253, 1674, 1362, 1256, 1182, 1140, 1073, 1015, 897 cm $^{-1}$; EIMS m/z (rel intens) 209 (M$^+$, 37), 182 (23), 164 (44), 128 (100), 111 (12), 99 (24), 86 (6), 70 (11); HRMS m/z (M$^+$) for $C_{10}H_{11}NO_4$, calcd 209.0688. found 209.0685; Anal. Calcd for $C_{10}H_{11}NO_4$: C, 57.42; H, 5.30; N, 6.70. Found: C, 57.06; H, 5.26; N, 6.40.

2-Ethoxycarbonyl-6,6-dimethyl-4,5,6,7-tetrahydrobenzoxazol-4-one (34) and 2-cyano-2-ethoxy-6,6-dimethyl-4,5,6,7-tetrahydrobenzodioxol-4-one (35)

Reaction of 2-diazo-5,5-dimethylcyclohexane-1,3-dione (166 mg, 1.0 mmol) with ethyl cyanoformate (3 mL) using rhodium acetate (8.8 mg, 0.02 mmol) as a catalyst afforded **34** (95 mg, 40 %) and **35** (100 mg, 42 %) as a mixture. **34:** mp 95-96℃; ^{1}H NMR δ 4.44 (2H, q, J= 7.1 Hz), 2.89 (2H, s), 2.49 (2H, s), 1.40 (3H, t, J= 7.1 Hz), 1.16 (6H, s); IR (KBr) 2962, 1745, 1703, 1401, 1278, 1223, 1182, 1151, 1050, 848 cm $^{-1}$; Anal. Calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90. Found: C, 61.07; H, 6.51; N, 5.75. **35:** ^{1}H NMR δ 3.81 (2H, m), 2.56-2.23 (4H, m), 1.27 (3H, m), 1.11 (3H, s), 1.03 (3H, s); IR (neat) 2965, 2253, 1684, 1373, 1352, 1175, 1086, 1067, 812 cm $^{-1}$.

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