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Carbenoid Insertion into the Peroxide Bond vs the Olefin Bond of Cyclic Peroxides

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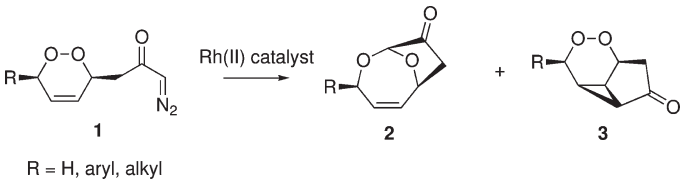

Herein we report examples of the insertion of a carbenoid into a peroxide linkage. This study reveals that intramolecular insertion of carbenes into the peroxide linkage of 3,6-dihydro-1,2-dioxines is preferred over olefin insertion. The initial scope of the reaction and mechanistic considerations, have been probed. This methodology also generates unusual bicyclic hemiacetals (**2**) and tricyclic peroxides (**3**).

Introduction

Post photo-oxidation modification reactions of compounds containing cyclic peroxide functionalities while maintaining the peroxide linkage intact are now becoming relatively common. The peroxide linkage exhibits stability to transformations such as cycloadditions,[1] reductions,[2] amidation,[3] and oxidations.[3,4] More rare are transformations on 3,6-dihydro-1,2-dioxines, as the presence of the olefin inherently makes any protons adjacent the peroxide linkage acidic, resulting in compounds highly sensitive to acidic and basic media. However, we are now finding that 3,6-dihydro-1,2-dioxines can be extremely robust moieties under the right conditions: stable to the oxidizing conditions of Jones' reagent,[4] allylations involving $TiCl_4$ or $SnCl_4$,[5] and DCC coupling.[6] The 3,6-dihydro-1,2-dioxines are not only stable to these quite harsh conditions; it is also possible to carry out transformations on the alkene of the 3,6-dihydro-1,2-dioxines while maintaining the peroxide linkage intact. Such examples are epoxidation,[7,8] bromination,[7,9] halohydrin formation,[10] iodo-cyclization of tethered carboxylic acids[4,11] and alcohols,[11] dihydroxylation,[12−14] and cycloadditions.[15] In the past decade, our group has noted this stability, and we are now making inroads into investigating such transformations of 1,2-dioxines.

One particular transformation that has intrigued us for over a decade[16] is the possible insertion of carbenes or carbenoids into the peroxide linkage or olefin unit of 3,6-dihydro-1,2-dioxines, Figure 1.

From our initial investigations a decade ago, it was clear that carbenoids generated intermolecularly did not insert into the peroxide linkage or for that matter into the alkene

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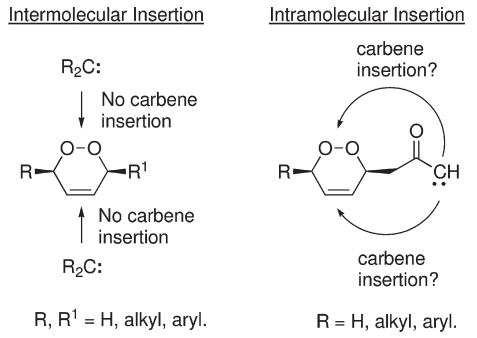
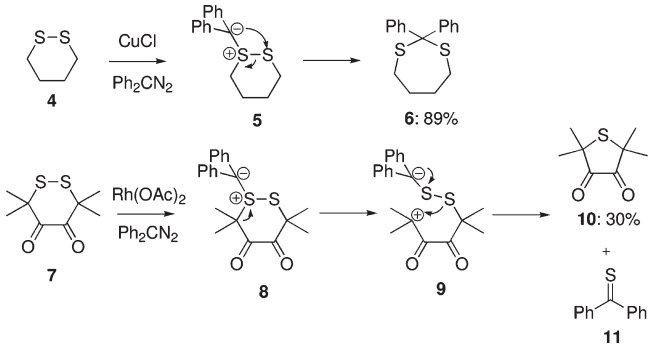


FIGURE 1. Possible sites of insertion of carbenes into 3,6-dihydro-1,2-dioxines.

SCHEME 1



unit of 3,6-dihydro-1,2-dioxines (**1**). Instead, dimerization of the carbenoids and the formation of furans and 1,4-dicarbonyls, derived from the 3,6-dihydro-1,2-dioxines, were noted. These latter products are in fact due to a competing Kornblum−DeLaMare rearrangement of the 3,6-dihydro-1,2-dioxines and are induced by the presence of base within the reaction medium.[17] We found this result surprising as it is known that carbenoids insert into the disulfide bond of 3,6-dihydro-1,2-dithianes in good yield, Scheme 1.[18,19] Cyclic disulfides (**4** and **7**) have been allowed to react in the presence of carbenes (intermolecularly), resulting in the insertion of the carbene into the disulfide linkage, top equation, Scheme 1. Alternatively, rearrangement via cleavage of the carbon−sulfur bond leading to cyclic thioethers has been demonstrated, bottom equation, Scheme 1. The mechanism for this reaction is proposed as a two-step process with initial formation of the sulfur ylide (**5** and **8**) followed by one of two rearrangements.

We now believe that our previous attempts were constrained and not optimal to examine carbene insertions into the peroxide or olefin moieties of 3,6-dihydro-1,2-dioxines as the reaction conditions were inherently basic. Thus, we have now turned our attention to examining the same processes intramolecularly as depicted in Figure 1.

Recently, within the group, we have generated methods for easy manipulation of tethered hydroxyl 1,2-dioxines into carboxylic acids.[11] We therefore were in a prime position to evaluate the possible intramolecular insertion of carbenes

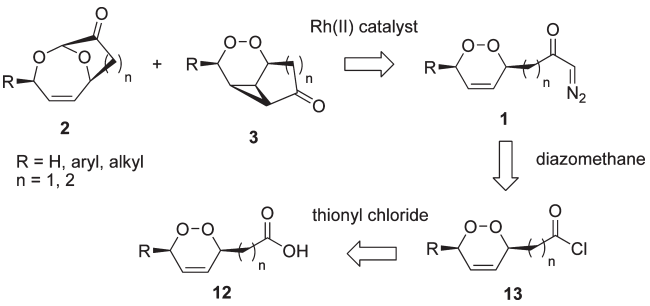


FIGURE 2. Retrosynthetic route to evaluate intramolecular carbenoid insertion into the peroxide/olefin moieties of 3,6-dihydro-1,2-dioxines (**1**).

into the olefin/peroxide moieties of 3,6-dihydro-1,2-dioxines. It was our proposal to transform the carboxylic acids (**12**) into acid chlorides (**13**) and then derivatize these as diazoketones (**11**) using diazomethane. We believed these transformations would be suitably mild to allow maintenance of the peroxide linkage intact. Rhodium-catalyzed decomposition of diazoketones occurs extremely rapidly, and therefore, the formation of and subsequent reaction of the rhodium carbenoid would occur far more rapidly than rhodium-catalyzed decomposition of the peroxide linkage.[20] This would give us a strategy for probing the potential cyclizations of carbenoids into the olefin/peroxide units of 3,6-dihydro-1,2-dioxines (**1**), Figure 2.

Results and Discussion

Synthesis of the requisite carboxylic acids (**12**) from hydroxyl-tethered 3,6-dihydro-1,2-dioxines was carried out via oxidation of the corresponding alcohol as previously reported.[11] Acid chlorides (**13**) were generated employing thionyl chloride, Scheme 2. Without further purification, diazoesters were generated in moderate yields over the two steps by the addition of freshly distilled diazomethane, Scheme 2, Table 1.

SCHEME 2

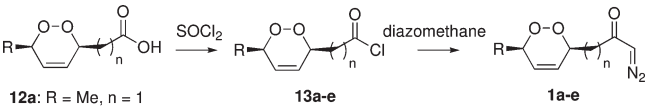


TABLE 1. Diazoester Formation

entry	carboxylic acid	diazoester (isolated yield, %)
1	**12a**	**1a** (50)
2	**12b**	**1b** (54)
3	**12c**	**1c** (55)
4	**12d**	**1d** (61)
5	**12e**	**1e** (49)

With the diazoesters **1a**−**e** in hand, all were allowed to react with catalytic amounts of rhodium(II) acetate dimer in dichloromethane, Scheme 3. Treatment of 3,6-dihydro-1,2-dioxine **1a** with rhodium(II) acetate dimer resulted in

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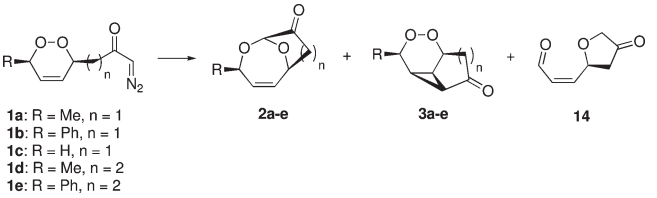
TABLE 2. Rhodium-Catalyzed Cyclization of Diazoesters 1a−e

entry	diazoester	products **2**:**3**:**14** (% yield)
1	**1a**	41:14:0
2	**1b**	62:11:0
3	**1c**	32:0:8
4	**1d**	
5	**1e**	

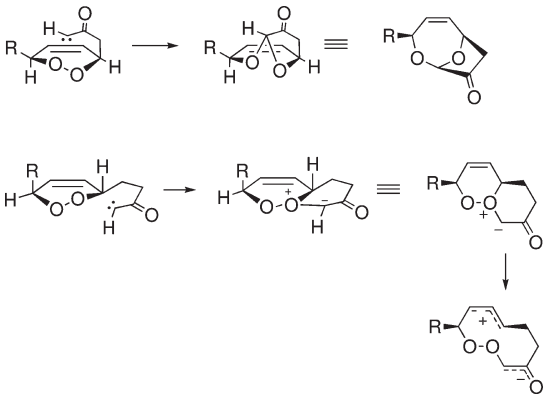
SCHEME 3



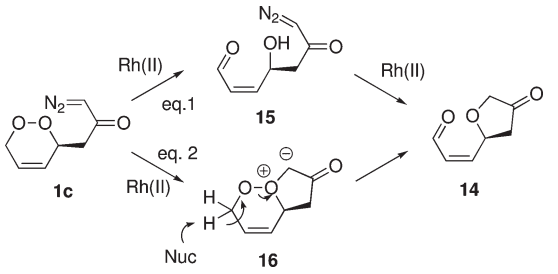
decomposition of the diazoketone tether and formation of two products in moderate yields, Table 2, entry 1. On the basis of the 1D and 2D NMR analyses, the two products formed were found to be a result of either insertion of the carbenoid into the peroxide linkage (**2a**) or olefin (**3a**) of 3,6-dihydro-1,2-dioxine **1a** with a ratio of 3:1, respectively, Scheme 3. All of the expected resonances for **2a** were observed with resonances at 5.68 ppm due to the olefin and a singlet at 5.02 ppm due to the proton attached to the cyclic hemiacetal. This latter observation confirms insertion into the peroxide linkage. In addition, ^{13}C NMR showed the expected alkene signals at 136.43 and 131.67 ppm and a signal at 93.74 ppm due to the carbon of the cyclic hemiacetal. The minor product formed through insertion of the tether into the olefin bond was cyclopropane **3a**. ^{1}H NMR of the cyclopropane showed resonances in the region of 1.58−2.05 ppm due to the newly formed cyclopropane ring. Furthermore, the lack of resonances in the region 5.89−5.93 ppm confirmed the loss of the olefin moiety. ^{13}C NMR confirmed the loss of the olefin moiety and formation of the cyclopropane ring as well as two resonances at 74.8 and 71.8 ppm confirming the presence of the peroxide linkage. A similar cyclization profile was observed for 3,6-dihydro-1,2-dioxines **1b** and **1c**; however, reaction of **1c** gave no cyclopropane with a small amount of aldehyde **14** also found.

For 3,6-dihydro-1,2-dioxines (**1d** and **1e**) where $n = 2$ a complex mixture of products was observed with no indication of the formation of **2d**,**e** or **3d**,**e**. We hypothesize that the reason for the complex mixture of products is due to a difference in the interaction of the carbenoid with the peroxide bond, Scheme 4. With the longer tether, cyclization of the generated carbene moves from the more concerted mechanism of the shorter tether outlined in the top equation of Scheme 4 to that of oxygen ylide formation outlined in the bottom equation of Scheme 4. Once the oxygen ylide is generated, cyclization to the hemiacetal is sterically restricted and charge separation favored. The charge separation generates a highly reactive intermediate which could undoubtedly be responsible for the numerous products isolated from these reactions. Indeed, formation of the oxygen ylide must be so favorable that there was no evidence of cyclopropane formation. This mirrors the modes of reaction observed in insertion of carbenes into disulfide linkages, summarized in Scheme 1.

SCHEME 4



SCHEME 5



The isolation of 8% of **14** from the reaction of **1c** with rhodium(II) acetate dimer, could arise through the Rh(II)-catalyzed formation of *cis*-γ-hydroxy enone **15**[20] and cyclization of the carbenoid into the electron rich O−H bond,[21,22] eq 1, Scheme 5. Alternatively, this could be the result of intermolecular decomposition of the oxygen ylide **16**, eq 2, Scheme 5, initiated by the basic reaction medium.

Conclusion

Within this study, we have shown the first examples of the insertion of a carbenoid into the peroxide linkage of 3,6-dihydro-1,2-dioxines. The initial scope of the reaction and mechanistic considerations, have been probed. This study reveals that intramolecular insertion of carbenes into the peroxide linkage of 3,6-dihydro-1,2-dioxines is preferred over olefin insertion allowing for generation of unusual bicyclic hemiacetals (**2**) and tricyclic peroxides (**3**).

Experimental Section

General Methods. Solvents were dried and purified where needed and according to literature methods. Thin layer chromatography (TLC) was performed using silica gel F_{254} (30 mm × 60 mm) and visualized under 254 nm light or developed in vanillin or permanganate dip. Flash chromatography was conducted using silica gel 60 of particle size 0.040−0.063 mm. ^{1}H NMR and ^{13}C NMR spectra were obtained in deuterated chloroform. TMS (0 ppm) and $CDCl_3$ (77.00 ppm) were used as internal standards for ^{1}H NMR and ^{13}C NMR analysis, respectively. Melting points are uncorrected. Infrared spectra were recorded as either Nujol mulls or neat as denoted. All yields

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reported are isolated yields judged to be homogeneous by TLC and NMR spectroscopy.

General Procedure for the Synthesis of 3,6-Dihydro-1,2-dioxines 12a−c. To a solution of the respective 3,6-dihydro-1,2-dioxine (1 equiv) in acetonitrile/water (1: 1, 20 mL/1.0 g of 1,2-dioxine) were added BAIB (2.2 equiv) and TEMPO (0.2 equiv) in a single portion, and the mixture was protected from light and stirred until the reaction was complete by TLC. The reaction mixture was extracted with ethyl acetate (4×) followed by 5% $NaHCO_3$ (4×). The aqueous solution was acidified using concentrated HCl and extracted with ethyl acetate (4×). The organic layer was then dried ($MgSO_4$) and filtered, and the volatiles were removed in vacuo. The crude residue was purified by column chromatography to afford the desired 3,6-dihydro-1,2-dioxines **12a−c**. 3,6-Dihydro-1,2-dioxines **12a**[11] and **12b**[11] have previously been reported.

(±) (3*S*)-3,6-Dihydro-1,2-dioxin-3-ylacetic acid (12c): yield 701 mg, 53% as white crystals; mp 82−84 °C; R_f 0.43 (2:3 ethyl acetate/hexane); ν_{max} (Nujol)/cm^{-1} 3200−2359, 1714, 1192, 1194, 1064; δ_H(300 MHz; $CDCl_3$) 2.68 (1H, dd, J = 16.28, 5.50 Hz), 2.88 (1H, dd, J = 16.29, 7.97 Hz), 4.42−4.50 (1H, m), 4.64−4.71 (1H, m), 4.91−4.96 (1H, m), 5.97−6.01 (2H, m); δ_C(75 MHz; $CDCl_3$) 176.6, 126.0, 125.3, 74.7, 69.8, 37.8; *m*/*z* (EI) (M^+ 144, 1), 126 (50), 81 (100), 53 (30); HRMS calcd for ($M^+ + Na^+$) $C_6H_8O_4Na$ requires 167.0320, found 167.0323.

General Procedure for the Synthesis of 1,2-Dioxines 12d,e. To a solution of respective 3,6-dihydro-1,2-dioxine (1 equiv) in acetone (20 mL/1.0 g of 1,2-dioxine) at 0 °C was added 2.67 M Jones reagent dropwise, and the solution was allowed to stir for 30 min at 0 °C then 1.5 h at ambient temperature. To the solution was added water and the resulting solution extracted with ethyl acetate (4×). The organic layer was washed with water until the yellow color subsided, followed by brine (2×), dried ($MgSO_4$), and filtered, and the volatiles were removed in vacuo. The crude residue was purified by column chromatography to afford the desired 1,2-dioxines **12d**,**e**.

(±)-3-[(3*S*,6*R*)-6-Methyl-3,6-dihydro-1,2-dioxin-3-yl]propanoic acid (12d): yield 1 g, 58% as a yellow oil; R_f 0.29 (2:3 ethyl acetate/hexane); ν_{max} (film)/cm^{-1} 3044, 1714, 1445, 1260, 1052; δ_H (300 MHz; $CDCl_3$) 1.24 (3H, d, J = 6.73 Hz), 1.92−2.21 (2H, m), 2.35−2.58 (2H, m), 4.32−4.75 (1H, m), 4.70 (1H, dq, J = 1.59, 6.68 Hz), 5.89 (2H, s); δ_C (75 MHz; $CDCl_3$) 179.5, 129.7, 126.5, 76.9, 74.3, 29.8, 27.8, 17.9; *m*/*z* (EI) (M^+ 172, 1), 154 (25), 108 (8), 96 (100); HRMS calcd for ($M^+ - H$) $C_8H_{11}O_4$ requires 171.0657, found 171.0657.

(±)-3-[(3*S*,6*S*)-6-Phenyl-3,6-dihydro-1,2-dioxin-3-yl]propanoic acid (12e): yield 750 mg, 56% as a white needles; δ_H (300 MHz; $CDCl_3$) 2.36−1.82 (2H, m), 2.94−2.38 (2H, m), 4.59 (1H, dd, J = 8.68, 3.34 Hz), 5.58 (1H, s), 6.11 (2H, s), 7.38 (5H, m); δ_C (75 MHz; $CDCl_3$) 179.1, 136.8, 129.0, 128.6, 128.6, 127.8, 127.4, 80.4, 77.1, 29.7, 27.9; remaining physical and chemical properties as per literature.[23]

General Procedure for the Synthesis of Diazoketones 1a−e. The respective 1,2-dioxines (1 equiv) in thionyl chloride (20 mL/1.0 g of 1,2-dioxine) were stirred for 24 h, and then the volatiles were carefully removed in vacuo and the acid chlorides used without further purification. Into a solution of the acid chloride (1 equiv) in ether (20 mL/g of acid chloride) was directly distilled diazomethane in ether, derived from reaction of diazald (67 equiv) with KOH solution in carbitol and ether. The mixture was allowed to stir at ambient temperature for 24 h. Volatiles were removed in vacuo, and the crude residue was purified by column chromatography to afford the desired diazoketones **1a−e**.

(±)-1-Diazo-3-[(3*S*,6*R*)-6-methyl-3,6-dihydro-1,2-dioxin-3-yl]-acetone (1a): yield 57 mg, 50% yellow oil; R_f 0.41 (2:3 ethyl acetate/hexane); ν_{max} (film)/cm^{-1} 2981, 2933, 2105, 1633, 1039; δ_H (300 MHz; $CDCl_3$) 1.22 (3H, d, J = 6.77 Hz), 2.55 (1H, dd, J = 14.82, 3.26 Hz), 2.87 (1H, dd, J = 14.16, 8.09 Hz), 4.75−4.87 (2H, m), 5.39 (1H, bs), 5.87−5.97 (2H, m); δ_C (75 MHz; $CDCl_3$) 191.7, 129.9, 126.3, 75.1, 74.4, 55.8, 44.4, 17.6; *m*/*z* (EI) (M^+ 182, 1), 154 (5), 110 (14), 81 (100), 67 (30), 55 (30); HRMS calcd for ($M^+ + Na^+$) $C_8H_{10}N_2O_3Na$: requires 205.0589, found 205.0586.

(±)-1-Diazo-3-[(3*S*,6*S*)-6-phenyl-3,6-dihydro-1,2-dioxin-3-yl]-acetone (1b): yield 120 mg, 54% yellow oil; R_f 0.55 (2:3 ethyl acetate/hexane); ν_{max} (film)/cm^{-1} 3103, 2104, 1644, 1372, 1142; δ_H (300 MHz; $CDCl_3$) 2.63 (1H, dd, J = 14.98, 4.10 Hz), 2.93 (1H, dd, J = 14.86, 8.16 Hz), 4.88−5.01 (1H, m), 5.36 (1H, s), 5.64 (1H, d, J = 1.59 Hz), 6.08−6.20 (2H, m), 7.32−7.40 (5H, m); δ_C (75 MHz; $CDCl_3$) 191.4, 136.1, 129.2, 128.6, 128.6, 127.6, 127.4, 80.5, 75.2, 55.8, 44.2; HRMS calcd for ($M^+ + Na^+$) $C_{13}H_{12}N_2O_3Na$ requires 267.0746, found 267.0748.

(±)-1-Diazo-3-[(3*S*)-3,6-dihydro-1,2-dioxin-3-yl]acetone (1c): yield 129 mg, 55% yellow oil; R_f 0.30 (2:3 ethyl acetate/hexane); ν_{max} (film)/cm^{-1} 3101, 2107, 1633, 1371, 1141; δ_H (300 MHz; $CDCl_3$) 2.42−2.62 (1H, m), 2.66−2.86 (1H, m), 4.33−4.49 (1H, m), 4.52−4.71 (1H, m), 4.83−5.00 (1H, m), 5.37 (1H, s), 5.85−6.07 (2H, m); δ_C (75 MHz; $CDCl_3$) 191.3, 126.6, 124.8, 75.4, 69.8, 55.6, 43.7; *m*/*z* (EI) (M^+ 168, 1%), 140(15), 111(100), 83(28), 55(85); HRMS calcd for ($M^+ + Na^+$) $C_7H_8N_2O_3Na$ requires 191.0433, found 191.0436.

(±)-1-Diazo-4-[(3*S*,6*S*)-6-methyl-3,6-dihydro-1,2-dioxin-3-yl]-butan-2-one (1d): yield 70 mg, 61% yellow oil; R_f 0.41 (2:3 ethyl acetate/hexane); ν_{max} (film)/cm^{-1} 2979, 2105, 1643, 1378, 1138; δ_H (300 MHz; $CDCl_3$) 1.24 (3H, d, J = 6.72 Hz), 1.75−2.13 (2H, m), 2.51 (2H, m), 4.41 (1H, dd, J = 6.87, 5.13 Hz), 4.69 (1H, dq, J = 6.70, 1.72 Hz), 5.33 (1H, s), 5.88 (2H, s); δ_C (75 MHz; $CDCl_3$) 194.3, 129.3, 126.8, 77.1, 74.2, 54.5, 36.3, 27.9, 17.9; *m*/*z* (EI) (M^+ 196, 1), 168 (15), 125 (60), 97 (70), 55 (100); HRMS calcd for ($M^+ + Na^+$) $C_9H_{12}N_2O_3Na$ requires 219.0746, found 219.0737.

(±)-1-Diazo-4-[(3*S*,6*S*)-6-phenyl-3,6-dihydro-1,2-dioxin-3-yl]-butan-2-one (1e): yield 90 mg, 49% yellow oil; R_f 0.50 (2:3 ethyl acetate/hexane); ν_{max} (film)/cm^{-1} 3101, 2104, 1634, 1379, 1070; δ_H (300 MHz; $CDCl_3$) 1.92−2.22 (2H, m), 2.50 (1H, s), 4.45−4.77 (2H, m), 5.25 (1H, s), 5.39−5.65 (1H, m), 6.00−6.25 (2H, m), 7.36 (5H, s); δ_C (75 MHz; $CDCl_3$) 194.1, 136.8, 128.9, 128.5, 128.5, 128.0, 126.9, 80.2, 77.3, 54.6, 36.2, 27.9; *m*/*z* (EI) (M^+ 258, 75), 213 (25), 170 (100), 157 (85), 128 (25), 77 (10); HRMS calcd for ($M^+ + Na^+$) $C_{14}H_{14}N_2O_3Na$ requires 281.0902, found 281.0893.

General Procedure for Cyclization: Synthesis of 2a−e, 3a−e, and 14. To a solution of the respective diazoketones in dichloromethane (1 mL/1 g of diazoketone) was added $Rh_2(OAc)_4$ (10% by weight) in one portion and the mixture stirred for 10 min. Volatiles were removed in vacuo, and the crude residue was purified by column chromatography to afford compounds **2a−c**, **3a**, **b**, and **14**.

(±)-(3*R*,6*S*)-3-Methyl-2,9-dioxabicyclo[4.2.1]non-4-en-8-one (2a) and (±)-(3*R*,5a*S*)-3-methylhexahydro-4*H*-1,2-dioxacyclopropa[*cd*]inden-4-one (3a): yield 16 mg, 55% as a yellow oil. **(±)-(3*R*,6*S*)-3-Methyl-2,9-dioxabicyclo[4.2.1]non-4-en-8-one (2a):** yield 12 mg, 41%; R_f 0.75 (2:3 ethyl acetate/hexane); ν_{max} (film)/cm^{-1} 2987, 2936, 1771, 1037; δ_H (600 MHz; $CDCl_3$) 1.31 (3 H, d, J = 6.94 Hz), 2.43 (1H, ddd, J = 18.08, 2.11, 0.84 Hz), 2.60 (1H, dd, J = 18.08, 8.97 Hz), 4.78 (1H, dq, J = 6.94, 1.57 Hz), 5.02 (1H, s), 5.19 (1H, m), 5.68 (2H, m); δ_C (150 MHz; $CDCl_3$) 205.9, 136.4, 131.7, 93.7, 78.1, 66.4, 38.6, 21.3; *m*/*z* (EI) (M^+ 154, 1), 126 (35), 108 (33), 83 (80), 79 (100), 55 (80); HRMS calcd for ($M^+ + Na^+$) $C_8H_{10}O_3Na$ requires 177.0528, found 177.0524. **(±)-(3*R*,5a*S*)-3-Methylhexahydro-4*H*-1,2-dioxacyclopropa[*cd*]-inden-4-one (3a):** yield 4 mg, 14%; R_f 0.30 (2:3 ethyl acetate/hexane); ν_{max} (film)/cm^{-1} 2995, 2932, 1732, 1099; δ_H (600 MHz; $CDCl_3$) 1.21 (3H, d, J = 6.38 Hz), 2.05 (1H, dd, J = 9.24,

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5.33 Hz), 2.70 (3H, m), 4.66 (1H, dq, J = 6.36, 2.11 Hz), 4.89 (1H, ddd, J = 6.38, 4.48, 2.20 Hz); δ_C (75 MHz; $CDCl_3$) 210.3, 74.8, 71.8, 49.1, 32.2, 28.3, 26.5, 17.9; m/z (EI) (M^+ 154, 1), 136 (31), 109 (62), 94 (100), 66 (62), 55 (31); HRMS calcd for ($M^+ + Na^+$) $C_8H_{10}O_3Na$: requires 177.0528, found 177.0526.

(±)-(3*S*,6*S*)-3-Phenyl-2,9-dioxabicyclo[4.2.1]non-4-en-8-one (2b) and (±)-(3*S*,5a*S*)-3-phenylhexahydro-4*H*-1,2-dioxacyclopropa[*cd*]inden-4-one (3b): yield 60.3 mg, 73% as yellow oil. **(±)-(3*S*,6*S*)-3-Phenyl-2,9-dioxabicyclo[4.2.1]non-4-en-8-one (2b):** yield 51 mg, 62%; R_f 0.67 (2:3 ethyl acetate/hexane); ν_{max} (film)/cm^{-1} 2952, 1767, 1454, 1104, 1020; δ_H (300 MHz; $CDCl_3$) 2.53 (1H, dd, J = 18.13, 1.88 Hz), 2.67 (1H, dd, J = 18.13, 8.69 Hz), 5.16 (1H, s), 5.21−5.37 (1H, m), 5.66 (1H, d, J = 1.68 Hz), 5.76−5.96 (2H, m), 7.19−7.69 (5H, m); δ_C (75 MHz; $CDCl_3$) 205.3, 140.9, 136.1, 132.5, 128.5, 127.8, 126.7, 93.8, 78.0, 72.3, 38.4; m/z (EI) (M^+ 216, 1), 170 (31), 145 (51), 128 (100), 115 (62), 91 (28); HRMS calcd for ($M^+ + Na^+$) $C_{13}H_{12}O_3Na$ requires 239.0684, found 239.0681. **(±)-(3*S*,5a*S*)-3-Phenylhexahydro-4*H*-1,2-dioxacyclopropa[*cd*]inden-4-one (3b):** yield 9.3 mg, 11%; R_f 0.27 (2:3 ethyl acetate/hexane); ν_{max} (film)/cm^{-1} 2918, 1731, 1455, 1280; δ_H (300 MHz; $CDCl_3$) 1.97−2.14 (1H, m), 2.25 (1H, dd, J = 9.13, 5.45 Hz), 2.61−2.95 (3H, m), 4.94−5.10 (1H, m), 5.56 (1H, d, J = 1.73 Hz), 7.14−7.56 (5H, m); δ_C (75 MHz; $CDCl_3$) 210.4, 135.8, 129.4, 128.8, 128.6, 78.3, 74.9, 48.9, 33.7, 27.6, 26.0; m/z (EI) (M^+ 216, 10), 170 (100), 141 (85), 115 (70), 105 (75), 77 (48); HRMS calcd for ($M^+ + Na^+$) $C_{13}H_{12}O_3Na$ requires 239.0684, found 239.0684.

(±)-(6*S*)-2,9-Dioxabicyclo[4.2.1]non-4-en-8-one (2c) and (±)-(2*Z*)-3-(4-oxotetrahydrofuran-2-yl)acrylaldehyde (14): yield 36 mg, 40% as a yellow oil. **(±)-(6*S*)-2,9-Dioxabicyclo[4.2.1]non-4-en-8-one (2c):** yield 29 mg, 32%; R_f 0.67 (2:3 ethyl acetate/hexane); ν_{max} (film)/cm^{-1} 2921, 1769, 1405, 1107; δ_H (300 MHz; $CDCl_3$) 2.36−2.52 (1H, m), 2.65 (1H, dd, J = 18.10, 8.77 Hz), 4.11 (1H, dd, J = 18.10, 8.77 Hz), 4.41−4.57 (1H, m), 5.05 (1H, s), 5.18−5.26 (1H, m), 5.74−5.96 (2H, m); δ_C (75 MHz; $CDCl_3$) 206.7, 132.6, 130.8, 94.3, 77.8, 61.29, 38.9; m/z (EI) (M^+ 140, 5), 112 (70), 183 (93), 66 (90), 55 (100); HRMS calcd for ($M^+ + Na^+$) $C_7H_8O_3Na$ requires 163.0371, found 163.0374. **(±)-(2*Z*)-3-(4-Oxotetrahydrofuran-2-yl)acrylaldehyde (14):** yield 7 mg, 8%; R_f 0.44 (2:3 ethyl acetate/hexane); ν_{max} (film)/cm^{-1} 3499, 2923, 1760, 1688, 1175, 1058; δ_H (300 MHz; $CDCl_3$) 2.36 (1H, m), 2.84 (1H, dd, J = 17.83, 6.48 Hz), 3.94 (1H, d, J = 17.01 Hz), 4.17 (1H, d, J = 16.99 Hz), 5.47−5.60 (1H, m), 6.17 (1H, m), 6.59 (1H, dd, J = 11.55, 7.05 Hz), 10.06 (1H, d, J = 5.78 Hz); δ_C (75 MHz; $CDCl_3$) 212.5, 190.7, 147.1, 129.8, 74.5, 71.2, 42.7; MS and HRMS could not be obtained due to stability issues.

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Supporting Information Available: ^1H NMR spectra for compounds **1a**−**e**, **2a**−**c**, **3a**,**b**, **12c**−**e**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.