Efficient Synthesis of Five- and Seven-Membered-Ring Heterocycles by Rhodium(II)-Catalyzed [3+2] and [3+4] Cycloaddition of Diazodicarbonyl Compounds with Conjugated Dienes

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Keywords: Cycloaddition / Heterocycles / Homogeneous catalysis / Rhodium

Rhodium(II)-catalyzed reactions of diazodicarbonyl compounds with a variety of conjugated dienes have been examined. These reactions provide a simple and rapid route to dihydrofurans and dihydrooxepines with a variety of substituents on the ring. The formation of these products is interpreted in terms of a stepwise mechanism.

Introduction

Dihydrofurans[1] and dihydrooxepines[2] are important heterocyclic compounds that are widespread in nature. They are frequently found in many natural products arising from plants and marine organisms. Several dihydrofurans and dihydrooxepines have been associated with a variety of biological activities such as pharmaceutical agents, insecticides, antiulcer, antiarrhythmic, and antileukemic agents.[3] Although numerous synthetic methods for the preparation of dihydrofurans[4] and dihydrooxepines[5] have been reported, single-step annulation approaches still remain scarce.

The rhodium(II)-catalyzed decomposition of diazocarbonyl compounds has become an important method in the synthesis of five-membered heterocycles such as furans[6] and oxazoles.[7] However, the rhodium(II)-catalyzed reaction of cyclic diazodicarbonyl compounds with 1,3-butadienes has not been investigated. Although metal-catalyzed reactions of acyclic diazo compounds such as ethyl diazoacetate[8] and vinyl diazoacetate[9] with conjugated dienes have been reported by many groups, these reactions predominantly afforded cyclopropanes[8] and cycloadducts.[9] We have tried to develop a new methodology utilizing rhodium-catalyzed reactions of diazodicarbonyl compounds with several substrates such as nitriles, isocyanates, ketones, vinyl ethers, and halides.[10] Continuing our studies in the development of a new methodology, we investigated the rhodium-catalyzed reactions of cyclic diazodicarbonyl compounds with conjugated dienes as these reactions seemed ideal for the preparation of five- and seven-membered-ring heterocycles. We report here a new and efficient synthesis of dihydrofurans and dihydrooxepines starting from a number of diazodicarbonyl compounds (Figure 1).

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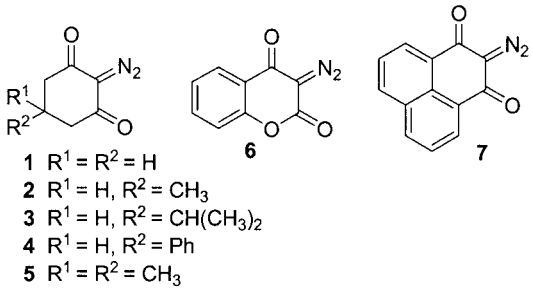
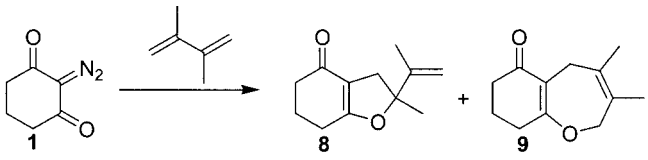


Figure 1. Diazodicarbonyl compounds.

Results and Discussion

In order to check the reactivity of diazodicarbonyl compounds with conjugated dienes, the reaction of **1** with 2,3-dimethyl-1,3-butadiene was first examined in the presence of several different metal catalysts (Table 1). No products were seen with $Cu(OAc)_2$ (1 mol%) or $Pd(OAc)_2$ (1 mol%) at room temperature. $Rh_2(OCOCF_3)_4$, $Rh_2(OAc)_4$, and $Rh_2(OPiv)_4$, however, showed catalytic activity, with Rh_2(O-

Table 1. Effect of metal catalysts in the reaction of **1** with 2,3-dimethyl-1,3-butadiene.



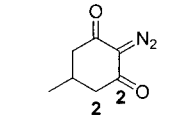
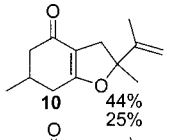
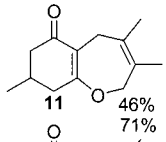
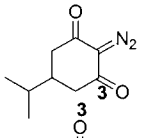
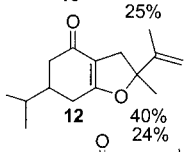
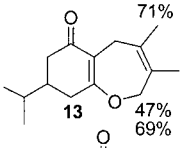
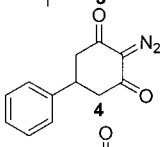
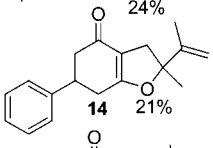
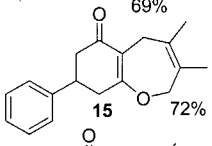
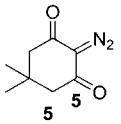
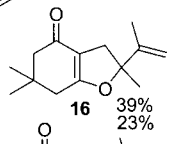
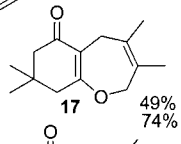
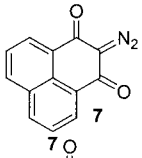
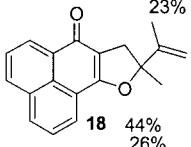
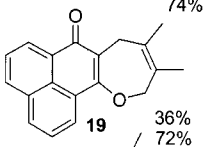
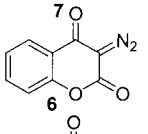
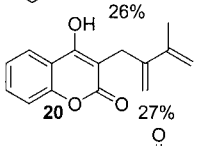
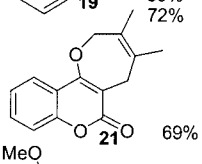
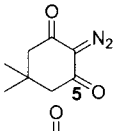
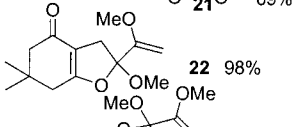
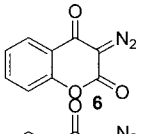
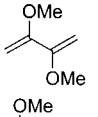
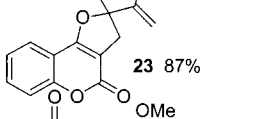
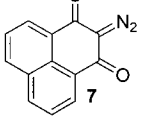
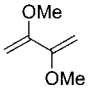
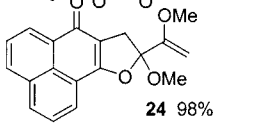
Catalyst	Condition	Yield [%] 8	9
$Cu(OAc)_2$	1 mol-%, room temp., 24 h	0	0
$Pd(OAc)_2$	1 mol-%, room temp., 24 h	0	0
$Rh_2(OCOCF_3)_4$	1 mol-%, room temp., 12 h	24	3
$Rh_2(OAc)_4$	1 mol-%, room temp., 6 h	43	40
$Rh_2(OPiv)_4$	0.5 mol-%, room temp., 3 h	23	73

  DOI: 10.1002/ejoc.200400452

Piv)$_4$ being a superior catalyst for seven-membered-ring formation. Reaction of **1** with 2,3-dimethyl-1,3-butadiene as both reactant and solvent in the presence of $Rh_2(OAc)_4$ (1 mol%, room temp., 6 h) gave dihydrofuran **8** (43%) and dihydrooxepine **9** (40%), whereas the reaction with Rh_2(OPiv)$_4$ (0.5 mol%, room temp., 3 h) afforded **8** (23%) and **9** (73%). When treated with **1** in several solvents such as dichloromethane, benzene, fluorobenzene, the side-products were compounds derived from carbene insertion. The two isomers were easily separated by column chromatography and assigned by spectroscopic analyses. The ^{1}H NMR spectrum of **8** shows two vinylic protons at δ = 4.97 (s, 1 H) and 4.82 ppm (s, 1 H) associated with the isopropenyl moiety on the dihydrofuran ring, whereas **9** shows two methylene peaks at δ = 4.62 (s, 2 H) and 3.20 ppm (s, 2 H) associated with the dihydrooxepine ring.

Additional reactions of diazodicarbonyl compounds **2**–**7** with symmetrical 1,3-butadienes such as 2,3-dimethyl-1,3-butadiene and 2,3-dimethoxy-1,3-butadiene were carried out with rhodium catalysts. The results are summarized in Table 2. Reaction of **2** with 2,3-dimethyl-1,3-butadiene in the presence of $Rh_2(OAc)_4$ gave dihydrofuran **10** (44%) and dihydrooxepine **11** (46%) as a mixture of isomers (entry 1). With rhodium pivalate, dihydrooxepine **11** was formed as a major component in 71% yield (entry 2). Other diazodicarbonyl compounds (**3**–**5** and **7**) provided similar results (entries 3–9). These reactions were more effective in terms of yield and selectivity for the formation of dihydrooxepines when rhodium pivalate was used as catalyst rather than rhodium acetate. However, treatment of **6** with 2,3-dimethyl-1,3-butadiene with $Rh_2(OPiv)_4$ as catalyst at 60 °C for 3 h gave the unexpected ring-opening product **20** (27%)

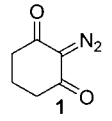
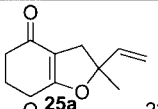
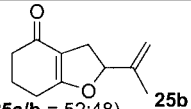
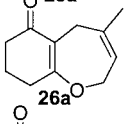
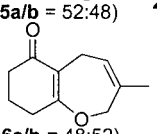
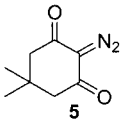
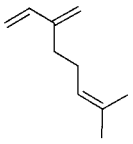
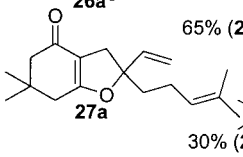
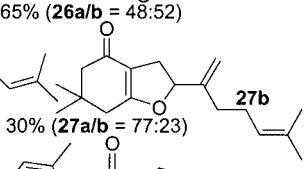
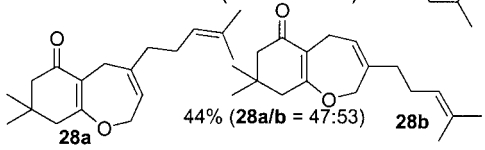
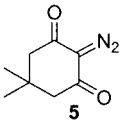
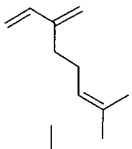
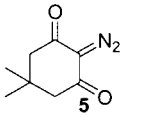
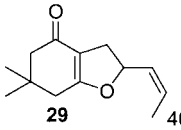
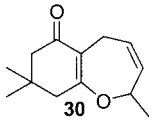
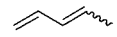
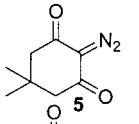
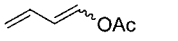
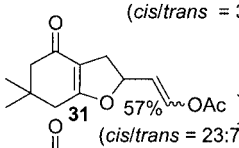
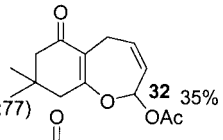
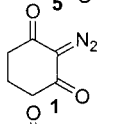
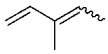
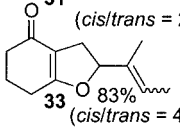
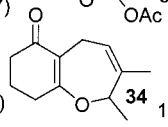
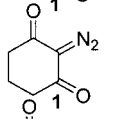
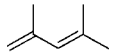
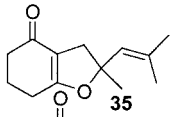
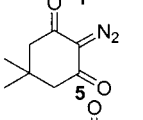
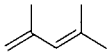
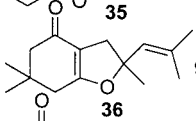
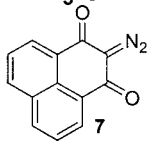
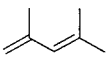
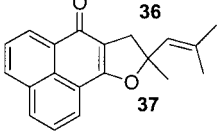
Table 2. Reactions of diazodicarbonyl compounds with symmetrical 1,3-butadienes. Method A: $Rh_2(OAc)_4$ (1 mol%, room temp., 6 h). Method B: $Rh_2(OPiv)_4$ (0.5 mol%, room temp., 3 h). Method C: $Rh_2(OPiv)_4$ (0.5 mol%, 60 °C, 3 h).

Entry	Diazodicarbonyl compound	1,3-Butadiene	Condition	Product (yield)
1			A	 **10** 44%  **11** 46%
2			B	25% 71%
3			A	 **12** 40%  **13** 47%
4			B	24% 69%
5			B	 **14** 21%  **15** 72%
6			A	 **16** 39%  **17** 49%
7			B	23% 74%
8			A	 **18** 44%  **19** 36%
9			B	26% 72%
10			C	 **20** 27%  **21** 69%
11			B	 **22** 98%
12			C	 **23** 87%
13			B	 **24** 98%

and dihydrooxepine **21** (69%; entry 10). On the other hand, in reactions with 2,3-dimethoxy-1,3-butadiene, a dramatic change was observed. When **5** was treated with 2,3-dimethoxy-1,3-butadiene in the presence of $Rh_2(OPiv)_4$, dihydrofuran **22** was formed in high yield (98%; entry 11). Similarly, other reactions also gave dihydrofurans **23** and **24** in 87 and 98% yields, respectively (entries 12 and 13). Interestingly, 2,3-dimethoxy-1,3-butadiene provides dihydrofurans as a sole product, probably due to the stabilization of the cation by the methoxy group.

In order to make a comparison with symmetrically conjugated dienes, unsymmetrical 1,3-butadienes were next examined. As shown in Table 3, treatment of **1** with isoprene in the presence of $Rh_2(OAc)_4$ gave dihydrofurans **25a** and **25b** (22%) and dihydrooxepines **26a** and **26b** (65%) as a mixture of four isomers (entry 1). The dihydrofurans **25a**

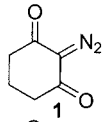
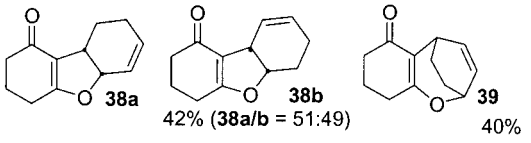
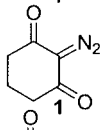
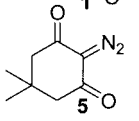
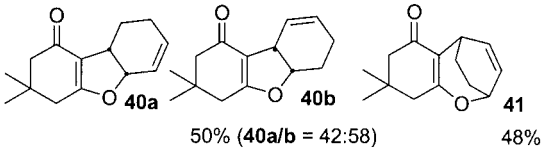
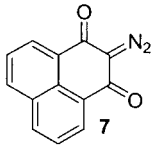
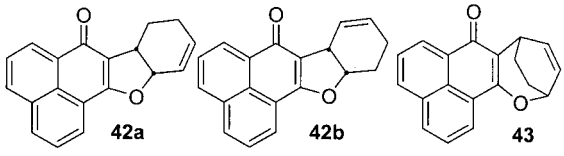
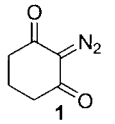
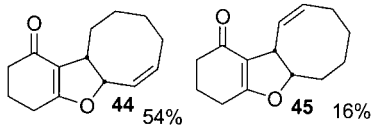
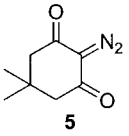
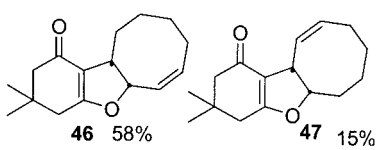
Table 3. Reactions of diazodicarbonyl compounds with unsymmetrical 1,3-butadienes. Method A: $Rh_2(OAc)_4$ (1 mol%, room temp., 6 h). Method B: $Rh_2(OPiv)_4$ (0.5 mol%, room temp., 3 h).

Entry	Diazodicarbonyl compound	1,3-Butadiene	Condition	Product (yield)
1	 **1**		A	 **25a**  **25b** 22% (**25a/b** = 52:48)  **26a**  **26b** 65% (**26a/b** = 48:52)
2	 **5**		A	 **27a**  **27b** 30% (**27a/b** = 77:23)  **28a** 44% (**28a/b** = 47:53) **28b**
3	 **5**		B	48% (**27a/b** = 33:67) 46% (**28a/b** = 63:37)
4	 **5**		B	 **29** 40%  **30** 51%
5	**5**	 (*cis*/*trans* = 50/50)	B	48% (*cis*/*trans* = 31:69) 50%
6	 **5**	 (*cis*/*trans* = 33/67)	B	 **31** 57% OAc (*cis*/*trans* = 23:77)  **32** OAc 35%
7	 **1**	 (*cis*/*trans* = 50/50)	B	 **33** 83% (*cis*/*trans* = 44:55)  **34** 16%
8	 **1**		B	 **35** 94%
9	 **5**		B	 **36** 93%
10	 **7**		B	 **37** 97%

and **25b** were easily separated from the dihydrooxepines **26a** and **26b** by column chromatography, but each individual component was not separable. The ratio of **25a** and **25b** to **26a** and **26b** was calculated by integration of the protons in the ^{1}H NMR spectra. Interestingly, in the case of 1,3-butadiene with a long chain, the reaction was also successful. Treatment of **5** with myrcene in the presence of $Rh_2(OAc)_4$ gave dihydrofurans **27a** and **27b** (30%) and dihydrooxepines **28a** and **28b** (44%) as a mixture (entry 2). This reaction was also repeated with $Rh_2(OPiv)_4$ to afford products **27a** and **27b** (48%) and **28a** and **28b** (46%) in increased yields (entry 3). With other unsymmetrical 1,3-dienes, the reactions were also successful. Reaction of **5** with *cis*-piperylene afforded dihydrofuran **29** (36%) and dihydrooxepine **30** (51%; entry 4). When the reaction was repeated with piperylene as a 1:1 ratio of stereoisomers, dihydrofuran **29** (48%) and dihydrooxepine **30** (51%) were isolated (entry 5). Similarly, with 1-acetoxy-1,3-butadiene as a 1:2 mixture of *cis*- and *trans*-isomers, dihydrofuran **31** (57%) and dihydrooxepine **32** (35%) were produced (entry 6). Reaction of **1** with 3-methyl-1,3-pentadiene as a 1:1 mixture of *cis*- and *trans*-isomers afforded dihydrofuran **33** (83%) and **34** (16%; entry 7). However, reaction of **1** with 2,4-dimethyl-1,3-pentadiene yielded dihydrofuran **35** (94%) without any formation of dihydrooxepine, probably due to the steric hindrance of the *gem*-dimethyl group (entry 8). Similarly, other diazodicarbonyl compounds **5** and **7** provided dihydrofurans **36** and **37** in high yields (entries 9 and 10). These reactions provide a rapid route for the preparation of dihydrofuran and dihydrooxepine derivatives with a variety of substituents on the dihydrofuran and dihydrooxepine rings.

Finally, reactions with cyclic 1,3-butadienes were examined. The results are summarized in Table 4. Treatment of **1** with 1,3-cyclohexadiene as both reactant and solvent in the presence of $Rh_2(OAc)_4$ resulted in dihydrofurans **38a** and **38b** (42%) and dihydrooxepine **39** (40%; (entry 1). When this reaction was repeated with $Rh_2(OPiv)_4$, a higher yield of products **38a** and **38b** (64%) was obtained (entry 2). The stereochemistry of **38a** and **38b** was assigned as *cis* by spectral analysis and by comparison with previously reported data.[10e] Further support for these structures was obtained from catalytic hydrogenation of **38a** and **38b** in the presence of Pd/C, which gives the same product, with a *cis* stereochemistry of the ring junction, after reduction of the double bond.[11] The methine proton of **38a** in the oxygen analog is observed at δ = 4.84 ppm (dd, J = 8.8,

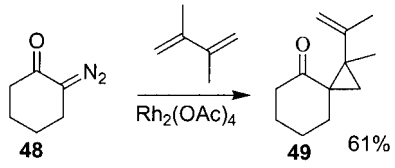
Table 4. Reactions of diazodicarbonyl compounds with cyclic 1,3-butadienes. Method A: $Rh_2(OAc)_4$ (1 mol%, room temp., 6 h). B: $Rh_2(OPiv)_4$ (0.5 mol%, room temp., 3 h).

Entry	Diazodicarbonyl compound	1,3-Butadiene	Condition	Product (yield)
1	 **1**		A	 **38a** **38b** 42% (**38a/b** = 51:49) **39** 40%
2	 **1**		B	64% (**38a/b** = 54:46) 33%
3	 **5**		B	 **40a** **40b** **41** 50% (**40a/b** = 42:58) 48%
4	 **7**		B	 **42a** **42b** **43** 82% (**42a/b** = 57:43) 16%
5	 **1**		B	 **44** 54% **45** 16%
6	 **5**		B	 **46** 58% **47** 15%

3.5 Hz), whereas that of **38b** appears at δ = 4.94 ppm (dt, J = 8.6, 3.5 Hz). The chemical shift of the methine proton in the oxygen analog of **39** is observed at δ = 4.67 ppm as a multiplet, and the two vinylic protons occur at δ = 6.63 (dd, J = 8.7, 7.4 Hz) and 5.99 ppm (dd, J = 8.7, 6.4 Hz), compared with δ = 6.17 and 5.91 ppm for **38a** and δ = 5.88 and 5.75 ppm for **38b**. Similarly, reactions of **5** and **7** with 1,3-cyclohexadiene afforded dihydrofurans as a mixture with dihydrooxepines (entries 3 and 4).

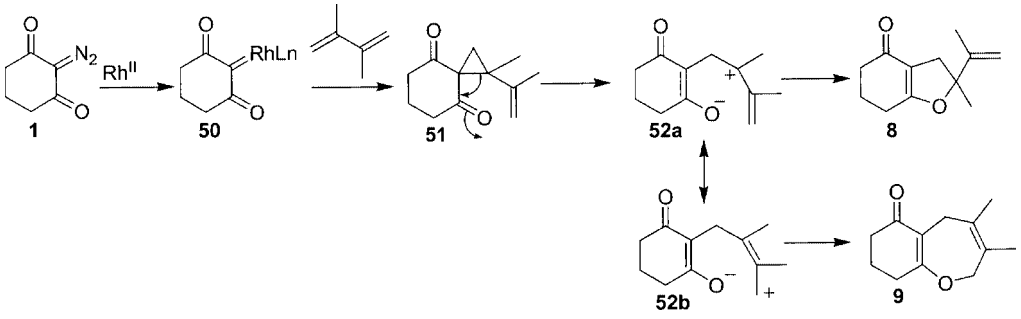
Reactions with eight-membered rings were also successful. Thus, treatment of **1** with *cis,cis*-1,3-cyclooctadiene in the presence of $Rh_2(OPiv)_4$ provided dihydrofurans **44** and **45** in 54 and 16% yields, respectively (entry 5). In this case, none of the expected dihydrooxepine was found. The stereochemistry of **44** and **45** was also assigned as *cis* by spectral analysis and by comparison with the products which were obtained from other CAN(IV)-mediated reactions.[12] The ^{1}H NMR spectrum of **44** shows a peak of the methine group next to the oxygen atom at δ = 5.29 as a doublet of doublets (J = 11.8, 4.0 Hz), whereas **45** shows a peak of the methine group next to the oxygen atom at δ = 4.66–4.58 as a multiplet. Similarly, reaction of **5** with *cis,cis*-1,3-cyclooctadiene gave products **46** (58%) and **47** (15%). These reactions provide a rapid entry to the synthesis of dihydrofuran and dihydrooxepine derivatives with a medium-sized ring on the dihydrofuran and dihydrooxepine skeletons.

Although the exact mechanism for the formation of dihydrofurans and dihydrooxepines is still not clear, it is best described as occurring via a cyclopropane intermediate, which was never isolated in these reactions. A mechanistic pathway involving a cyclopropane intermediate in rhodium-mediated reactions has already been proposed by several groups.[13] In order to observe a cyclopropane intermediate, reaction of the other diazo compound **48** was attempted with the rhodium catalyst. When **48** was treated with 2,3-dimethyl-1,3-butadiene as both reactant and solvent in the presence of 1 mol% of $Rh_2(OAc)_4$, cyclopropane adduct **49** was obtained as the sole product in 61% yield (Scheme 1). Interestingly, no other cycloadducts were isolated from this reaction. The structure of **49** was easily established by the chemical shifts of the methylene and methyl groups on the cyclopropane ring.

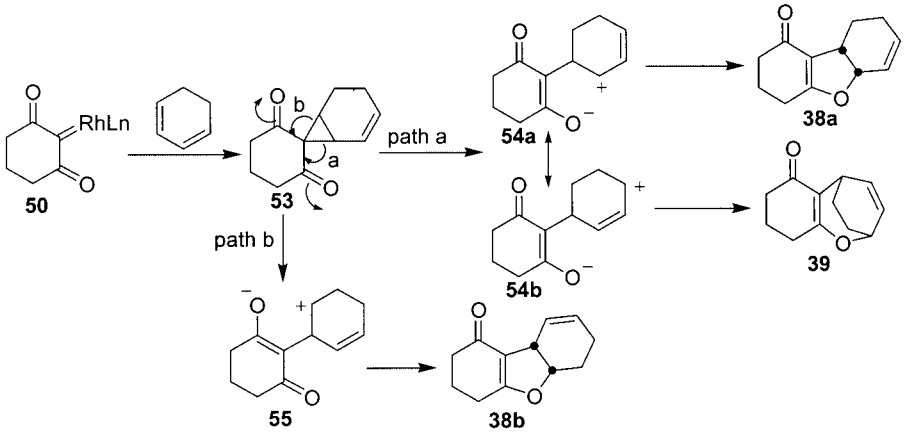


Scheme 1.

A mechanistic pathway accounting for our observations in Table 2 and Table 3 is shown in Scheme 2. The diazodicarbonyl compound **1** first gives a metal carbenoid **50** by displacement of nitrogen by the rhodium catalyst. Electrophilic carbenoid **50** is then attacked by the double bond of the 1,3-butadiene to give the cyclopropane intermediate **51**, which undergoes bond cleavage to give delocalized zwitterions **52a** and **52b**. Ring closure of these zwitterions gives



Scheme 2.



Scheme 3.

dihydrofuran **8** and dihydrooxepine **9**. Although an explanation for the preferred forrmation of dihydrooxepine over dihydrofuran in the presence of $Rh_2(OPiv)_4$ is not clear, this is likely to be due to the difference of relative reactivity of rhodium catalysts as a Lewis acid to the oxygen atom in the cyclization step.

The formation of cycloadducts (Table 4) can also be rationalized by a cyclopropane intermediate, as shown in Scheme 3. The cyclopropane intermediate **53** can undergo bond cleavage to give zwitterions **54a** and **54b** (path a) and **55** (path b). Ring closure of **54a** and **54b** gives dihydrofuran **38a** and dihydrooxepine **39**, while ring closure of **55** gives dihydrofuran **38b** with reverse regiochemistry.

In conclusion, reactions of diazodicarbonyl compounds with 1,3-butadienes have been carried out with a rhodium catalyst. The reactions easily provided a rapid entry to the synthesis of biologically interesting five- and seven-membered-ring heterocycles. This method may be useful in the synthesis of dihydrofurans and dihydrooxepines with a variety of substituents on the ring. The formation of these products is also described in terms of a stepwise mechanism.

Experimental Section

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 with microcover glasses on a Fisher–Johns apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker Model ARX (300 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Bruker Model ARX (75 MHz) spectrometer in $CDCl_3$ using δ = 77.0 ppm as the solvent chemical shift. IR spectra were recorded on a JASCO FTIR 5300 spectrophotometer. HRMS mass spectra were recorded by the Korea Basic Science Institute (Daegu).

General Procedure: $Rh_2(OAc)_4$ (0.01 mmol) or $Rh_2(OPiv)_4$ (0.005 mmol) was added at room temperature under a N_2 atmosphere to a solution of diazodicarbonyl compound (1.0 mmol)[14] and 1,3-butadiene (2 mL). The reaction mixture was stirred at room temperature for 3–6 h. The reaction mixture was then evaporated under reduced pressure to give a residue, which was purified by flash column chromatography on silica gel to give the product.

2-Isopropenyl-2-methyl-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one (8) and 3,4-Dimethyl-5,7,8,9-tetrahydro-2*H*-benzo[*b*]oxepin-6-one (9): Treatment of **1** (138 mg, 1.0 mmol) and 2,3-dimethyl-1,3-butadiene (2 mL) in the presence of $Rh_2(OPiv)_4$ (3 mg) afforded a mixture of **8** (44 mg, 23%) and **9** (140 mg, 73%) as a liquid.

8: R_f = 0.23 (*n*-hexane/ethyl acetate, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.48 (s, 3 H), 1.75 (s, 3 H), 1.98–2.07 (m, 2 H), 2.34 (t, ^3J = 6.9 Hz, 2 H), 2.43 (t, ^3J = 8.0 Hz, 2 H), 2.61 (d, ^2J = 14.4 Hz, 1 H), 2.82 (d, ^2J = 14.4 Hz, 1 H), 4.82 (s, 1 H), 4.97 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.5, 21.7, 24.0, 26.2, 36.4, 37.4, 93.4, 110.1, 112.5, 146.6, 176.1, 195.7 ppm. IR (neat): $\tilde{\nu}$ = 3096, 2946, 1636, 1453, 1400, 1370, 1252, 1186, 1125, 1053, 1001, 901, 856, 760 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{12}H_{16}O_2$ 192.1150; found 192.1153.

9: R_f = 0.43 (*n*-hexane/ethyl acetate, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.76 (s, 3 H), 1.78 (s, 3 H), 1.82–1.88 (m, 2 H), 2.27–2.34 (m, 4 H), 3.20 (s, 2 H), 4.62 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.1, 20.3, 27.9, 28.2, 30.9, 36.9, 72.0, 112.9, 126.4, 139.1, 173.91, 198.4 ppm. IR (neat): $\tilde{\nu}$ = 2984, 2946, 2874, 1643, 1601, 1431, 1393, 1298, 1265, 1186, 1128, 1105, 1067, 1013, 972, 949, 860 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{12}H_{16}O_2$ 192.1150; found 192.1148.

2-Isopropenyl-2,6-dimethyl-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one (10) and 3,4,8-Trimethyl-5,7,8,9-tetrahydro-2*H*-benzo[*b*]oxepin-6-one (11): Treatment of **2** (152 mg, 1 mmol) with 2,3-dimethyl-1,3-butadiene (2 mL) in the presence of $Rh_2(OAc)_{44}$ (4 mg) afforded **10** (91 mg, 44%) as a mixture of diastereomers and **11** (95 mg, 46%) as a liquid.

10: R_f = 0.22 (*n*-hexane/ethyl acetate, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (d, ^3J = 6.4 Hz, 3 H), 1.44 and 1.41 (3 H), 1.69 and 1.70 (3 H), 1.97–2.12 (m, 2 H), 2.16–2.47 (m, 3 H), 2.51–2.57 (m, 1 H), 2.73–2.78 (m, 1 H), 4.76 (s, 1 H), 4.92 and 4.90 (1 H) ppm. IR (neat): $\tilde{\nu}$ = 3096, 2957, 2872, 1634, 1402, 1233, 1022, 903 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{13}H_{18}O_2$ 206.1307; found 206.1309.

11: R_f = 0.48 (*n*-hexane/ethyl acetate, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (d, ^3J = 6.0 Hz, 3 H), 1.71 (s, 3 H), 1.73 (s, 3 H), 2.10–1.88 (m, 3 H), 2.35–2.40 (m, 2 H), 3.07 (d, ^2J = 17.8 Hz, 1 H), 3.21 (d, ^2J = 17.8 Hz, 1 H), 4.38 (d, ^2J = 12.1 Hz, 1 H), 4.78 (d, ^2J = 12.1 Hz, 1 H) ppm. IR (neat): $\tilde{\nu}$ = 2953, 2872, 1645, 1605, 1393, 1312, 1265, 1202, 1130, 1055, 920 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{13}H_{18}O_2$ 206.1307; found 206.1306.

2-Isopropenyl-6-isopropyl-2-methyl-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one (12) and 8-Isopropyl-3,4-dimethyl-5,7,8,9-tetrahydro-2*H*-benzo[*b*]oxepin-6-one (13): Treatment of **3** (180 mg, 1 mmol) with 2,3-dimethyl-1,3-butadiene (2 mL) in the presence of $Rh_2(OPiv)_4$ (3 mg) afforded **12** (56 mg, 24%) as a mixture of diastereomers and **13** (161 mg, 69%) as a liquid.

12: R_f = 0.27 (*n*-hexane/ethyl acetate, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (d, ^3J = 6.7 Hz, 6 H), 1.45 and 1.48 (3 H), 1.52–1.62 (m, 1 H), 1.70 and 1.74 (3 H), 1.93–2.22 (m, 3 H), 2.30–2.43 (m, 2 H), 2.58 (d, ^2J = 14.4 Hz, 1 H), 2.80 (d, ^2J = 14.4 Hz, 1 H), 4.46 and 4.47 (s, 1 H), 4.81 and 4.96 (1 H) ppm. IR (neat): $\tilde{\nu}$ = 3096, 2961, 2874, 1638, 1402, 1231, 1026, 903 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{15}H_{22}O_2$ 234.1620; found 234.1622.

13: R_f = 0.5 (*n*-hexane/ethyl acetate, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82 (d, ^3J = 6.7 Hz, 6 H), 1.37–1.49 (m, 1 H), 1.71 (s, 3 H), 1.74 (s, 3 H), 1.89–2.10 (m, 3 H), 2.18–2.25 (m, 1 H), 2.39–2.46 (m, 1 H), 3.06 (d, ^2J = 17.8 Hz, 1 H), 3.23 (d, ^2J = 17.8 Hz, 1 H), 4.34 (d, ^2J = 12.1 Hz, 1 H), 4.82 (d, ^2J = 12.1 Hz, 1 H) ppm. IR (neat): $\tilde{\nu}$ = 2961–2876, 1640, 1599, 1393, 1306, 1267, 1200, 1128. 1041 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{15}H_{22}O_2$ 234.1620; found 234.1621.

2-Isopropenyl-2-methyl-6-phenyl-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one (14) and 3,4-Dimethyl-8-phenyl-5,7,8,9-tetrahydro-2*H*-benzo-[*b*]oxepin-6-one (15): Treatment of **4** (214 mg, 1 mmol) with 2,3-dimethyl-1,3-butadiene (2 mL) in the presence of $Rh_2(OPiv)_4$ (3 mg) afforded **14** (56 mg, 21%) as a mixture of diastereomers and **15** (193 mg, 72%) as a liquid.

14: R_f = 0.26 (*n*-hexane/ethyl acetate, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.49 and 1.53 (3 H), 1.75 and 1.78 (3 H), 2.57–2.72 (m, 5 H), 2.85–2.91 (m, 1 H), 3.36–3.49 (m, 1 H), 4.82 and 4.84 (1 H), 4.97 and 5.00 (1 H), 7.23–7.35 (m, 5 H) ppm. IR (neat): $\tilde{\nu}$ = 3090, 3030, 2976, 2936, 1636, 1453, 1402, 1373, 1346, 1254, 1233, 1123, 1026, 905, 862 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{18}H_{20}O_2$ 268.1463; found 268.1461.

15: R_f = 0.49 (*n*-hexane/ethyl acetate, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.79 (s, 3 H), 1.80 (s, 3 H), 2.46–2.71 (m, 4 H), 3.14–

3.30 (m, 3 H), 4.42 (d, ^2J = 12.1 Hz, 1 H), 4.90 (d, ^2J = 12.1 Hz, 1 H), 7.18–7.34 (m, 5 H) ppm. IR (neat): $\tilde{\nu}$ = 3028, 2911, 1649, 1603, 1453, 1393, 1354, 1302, 1262, 1128, 1105, 1042, 970, 949, 906 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{18}H_{20}O_2$ 268.1463; found 268.1460.

2-Isopropenyl-2,6,6-trimethyl-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one (16) and 3,4,8,8-Tetramethyl-5,7,8,9-tetrahydro-2*H*-benzo[*b*]oxepin-6-one (17): Treatment of **5** (166 mg, 1 mmol) with 2,3-dimethyl-1,3-butadiene (2 mL) in the presence of $Rh_2(OPiv)_4$ (3 mg) afforded a mixture of **16** (51 mg, 23%) and **17** (163 mg, 74%) as a liquid.
16: R_f = 0.34 (*n*-hexane/ethyl acetate, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.07 (s, 3 H), 1.09 (s, 3 H), 1.48 (s, 3 H), 1.74 (s, 3 H), 2.20 (s, 2 H), 2.27 (s, 2 H), 2.60 (d, ^2J = 14.4 Hz, 1 H), 2.82 (d, ^2J = 14.4 Hz, 1 H), 4.81 (s, 1 H), 4.95 (s, 1 H) ppm. IR (neat): $\tilde{\nu}$ = 2957, 1638, 1404, 1242, 1167, 1146, 1121, 1030, 912 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{14}H_{20}O_2$ 220.1463; found 220.1464.
17: R_f = 0.55 (*n*-hexane/ethyl acetate, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.98 (s, 6 H), 1.75 (s, 3 H), 1.77 (s, 3 H), 2.14 (s, 2 H), 2.18 (s, 2 H), 3.19 (s, 2 H), 4.62 (s, 2 H) ppm. IR (neat): $\tilde{\nu}$ = 2959, 1649, 1609, 1449, 1391, 1304, 1262, 1217, 1165, 1128, 1042, 980, 905 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{14}H_{20}O_2$ 220.1463; found 220.1463.

9-Isopropenyl-9-methyl-8,9-dihydrophenaleno[1,2-*b*]furan-7-one (18) and 9,10-Dimethyl-8,11-dihydro-12-oxacyclohepta[*a*]phenalen-7-one (19): Treatment of **7** (222 mg, 1 mmol) with 2,3-dimethyl-1,3-butadiene (2 mL) in the presence of $Rh_2(OPiv)_4$ (3 mg) afforded a mixture of **18** (72 mg, 26%) and **19** (199 mg, 72%) as a liquid.
18: R_f = 0.27 (*n*-hexane/ethyl acetate, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.67 (s, 3 H), 1.86 (s, 3 H), 3.04 (d, ^2J = 15.4 Hz, 1 H), 3.25 (d, ^2J = 15.4 Hz, 1 H), 4.90 (s, 1 H), 5.13 (s, 1 H), 7.60 (t, ^3J = 7.8 Hz, 1 H), 7.71 (t, ^3J = 7.8 Hz, 1 H), 8.03–8.11 (m, 3 H), 8.60 (d, ^3J = 7.2 Hz, 1 H) ppm. IR (neat): $\tilde{\nu}$ = 2976, 1630, 1584, 1510, 1422, 1381, 1327, 1263, 1236, 1101, 1065, 1024, 901, 870, 845 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{19}H_{16}O_2$ 276.1150; found 276.1153.
19: R_f = 0.46 (*n*-hexane/ethyl acetate, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.86 (s, 6 H), 3.68 (s, 2 H), 4.95 (s, 2 H), 7.55 (t, ^3J = 7.8 Hz, 1 H), 7.66 (t, ^3J = 7.8 Hz, 1 H), 7.95 (d, ^3J = 8.1 Hz, 1 H), 8.07 (d, ^3J = 8.1 Hz, 1 H), 8.15 (d, ^3J = 7.3 Hz, 1 H), 8.53 (d, ^3J = 7.3 Hz, 1 H) ppm. IR (neat): $\tilde{\nu}$ = 3059, 2975, 2907, 2857, 1632, 1615, 1572, 1439, 1414, 1343, 1306, 1258, 1219, 1206, 1150, 1092, 986, 947, 843 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{19}H_{16}O_2$ 276.1150; found 276.1152.

4-Hydroxy-3-(3-methyl-2-methylenebut-3-enyl)chromenone (20) and 8,9-Dimethyl-7,10-dihydro-5,11-dioxacyclohepta[*a*]naphthalen-6-one (21): Treatment of **6** (188 mg, 1 mmol) with 2,3-dimethyl-1,3-butadiene (2 mL) in the presence of $Rh_2(OPiv)_4$ (3 mg) afforded **20** (65 mg, 27%) and **21** (167 mg, 69%).
20: R_f = 0.4 (*n*-hexane/ethyl acetate, 3:1). M.p. 133–134 °C (hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.86 (s, 3 H), 3.74 (s, 2 H), 5.09 (s, 1 H), 5.30 (s, 1 H), 5.36 (s, 1 H), 5.38 (s, 1 H), 7.01 (s, 1 H), 7.23–7.30 (m, 2 H), 7.51 (d, ^3J = 7.8 Hz, 1 H), 7.76 (d, ^3J = 7.8 Hz, 1 H) ppm. IR (KBr): $\tilde{\nu}$ = 3449, 3086, 2971, 1655, 1624, 1495, 1454, 1389, 1225, 1208, 1167, 1111, 1090, 965 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{15}H_{14}O_3$ 242.0943; found 242.0940.
21: Liquid. R_f = 0.57 (*n*-hexane/ethyl acetate, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.84 (s, 3 H), 1.86 (s, 3 H), 3.56 (s, 2 H), 4.93 (s, 2 H), 7.16–7.27 (m, 2 H), 7.43 (d, ^3J = 7.9 Hz, 1 H), 7.71 (d, ^3J = 7.9 Hz, 1 H) ppm. IR (neat): $\tilde{\nu}$ = 2976, 1705, 1611, 1570, 1491, 1456, 1397, 1325, 1204, 1109, 1044, 959, 758 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{15}H_{14}O_3$ 242.0943; found 242.0941.

2-Methoxy-2-(1-methoxyvinyl)-6,6-dimethyl-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one (22): Treatment of **5** (166 mg, 1 mmol) with 2,3-dimethoxy-1,3-butadiene (2 mL) in the presence of $Rh_2(OPiv)_4$ (3 mg) afforded **22** (247 mg, 98%) as a liquid. R_f = 0.67 (*n*-hexane/ethyl acetate, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08 (s, 3 H), 1.10 (s, 3 H), 2.21 (s, 2 H), 2.34 (s, 2 H), 2.82–3.01 (m, 2 H), 3.30 (s, 3 H), 3.61 (s, 3 H), 4.22 (s, 1 H), 4.41 (s, 1 H) ppm. IR (neat): 2961, 2839, 1644, 1454, 1404, 1352, 1321, 1260, 1238, 1208, 1084, 1024, 953, 899 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{14}H_{20}O_4$ 252.1362; found 252.1361.

2-Methoxy-2-(1-methoxyvinyl)-2,3-dihydrofuro[3,2-*c*]chromen-4-one (23): Treatment of **6** (188 mg, 1 mmol) with 2,3-dimethoxy-1,3-butadiene (2 mL) in the presence of $Rh_2(OPiv)_4$ (3 mg) afforded **23** (238 mg, 87%) as a liquid. R_f = 0.47 (*n*-hexane/ethyl acetate, 3:1). M.p. 129–130 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.27 (q, ^2J = 16,8 Hz, 2 H), 3.41 (s, 3 H), 3.66 (s, 3 H), 4.32 (d, ^2J = 2.9 Hz, 1 H), 4.68 (d, ^2J = 2.9 Hz, 1 H), 7.34–7.38 (m, 2 H), 7.71 (t, ^3J = 7.8 Hz, 1 H), 8.04 (d, ^3J = 7.8 Hz, 1 H) ppm. IR (KBr): $\tilde{\nu}$ = 2973, 2942, 1720, 1644, 1611, 1460, 1343, 1319, 1256, 1208, 1186, 1080, 1053, 1032, 924, 895 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{15}H_{14}O_5$ 274.0841; found 274.0844.

9-Methoxy-9-(1-methoxyvinyl)-8,9-dihydrophenaleno[1,2-*b*]furan-7-one (24): Reaction of **7** (222 mg, 1 mmol) with 2,3-dimethoxy-1,3-butadiene (2 mL) in the presence of $Rh_2(OPiv)_4$ (3 mg) afforded **24** (302 mg, 98%) as a solid. R_f = 0.7 (*n*-hexane/ethyl acetate, 1:1). M.p. 119–120 °C (hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.35 (q, ^2J = 17.1 Hz, 2 H), 3.44 (s, 3 H), 3.67 (s, 3 H), 4.31 (d, ^2J = 2.7 Hz, 1 H), 4.72 (d, ^2J = 2.7 Hz, 1 H), 7.62 (t, ^3J = 7.8 Hz, 1 H), 7.72 (t, ^3J = 7.8 Hz, 1 H), 8.14–8.05 (m, 3 H), 8.60 (d, ^3J = 7.3 Hz, 1 H) ppm. IR (KBr): $\tilde{\nu}$ = 3121, 3059, 2934, 1628, 1591, 1572, 1510, 1422, 1383, 1318, 1262, 1235, 1221, 1069, 1053, 1019, 968, 880 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{19}H_{16}O_4$ 308.1049; found 308.1047.

2-Methyl-2-vinyl-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one (25a), 2-Isopropenyl-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one (25b), 4-Methyl-5,7,8,9-tetrahydro-2*H*-benzo[*b*]oxepin-6-one (26a), and 3-Methyl-5,7,8,9-tetrahydro-2*H*-benzo[*b*]oxepin-6-one (26b): Treatment of **1** (138 mg, 1 mmol) with isoprene (2 mL) in the presence of $Rh_2(OAc)_4$ (4 mg) afforded **25a** and **25b** (39 mg, 22%) as a 52:48 ratio of isomers and **26a** and **26b** (116 mg, 65%) as a 48:52 ratio as inseparable mixtures.
25a: Liquid. R_f = 0.44 (*n*-hexane/ethyl acetate, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.49 (s, 3 H), 1.96–2.07 (m, 2 H), 2.33 (t, ^3J = 6.9 Hz, 2 H), 2.42 (t, ^3J = 7.8 Hz, 2 H), 2.64 (d, ^2J = 14.4 Hz, 1 H), 2.80 (d, ^2J = 14.4 Hz, 1 H), 5.10 (d, ^3J = 10.8 Hz, 1 H), 5.23 (d, ^3J = 17.3 Hz, 1 H), 5.95 (dd, ^3J = 17.3, ^3J = 10.8 Hz, 1 H) ppm.
25b: Liquid. R_f = 0.44 (*n*-hexane/ethyl acetate, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.71 (s, 3 H), 1.96–2.07 (m, 2 H), 2.33 (t, ^3J = 6.9 Hz, 2 H), 2.44 (t, ^3J = 7.8 Hz, 2 H), 2.59–2.64 (m, 1 H), 2.91–2.99 (m, 1 H), 4.89 (s, 1 H), 4.99 (s, 1 H), 5.17 (dd, ^3J = 10.5, ^3J = 2.3 Hz, 1 H) ppm. IR (neat) of **25a** and **25b**: $\tilde{\nu}$ = 2949, 1634, 1454, 1402, 1372, 1256, 1182, 1136, 1001, 901 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{11}H_{14}O_2$ 178.0994; found 178.0992.
26a: Liquid. R_f = 0.75 (*n*-hexane/ethyl acetate, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.79 (s, 3 H), 1.77–1.85 (m, 2 H), 2.27–2.34 (m, 4 H), 3.23 (s, 2 H), 4.59 (d, ^3J = 6.7 Hz, 2 H), 5.88 (t, ^3J = 6.7 Hz, 1 H) ppm.
26b: Liquid. R_f = 0.75 (*n*-hexane/ethyl acetate, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.80 (s, 3 H), 1.77–1.85 (m, 2 H), 2.27–2.34 (m, 4 H), 3.12 (d, ^3J = 6.7 Hz, 2 H), 4.62 (s, 2 H), 5.72 (t, ^3J = 6.7 Hz, 1 H) ppm. IR (neat) of **26a** and **26b**: $\tilde{\nu}$ = 2944, 1645, 1431, 1391, 1362, 1283, 1260, 1229, 1192, 1171, 1115, 1007, 954 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{11}H_{14}O_2$ 178.0994; found 178.0991.

6,6-Dimethyl-2-(4-methyl-pent-3-enyl)-2-vinyl-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one (27a), 6,6-Dimethyl-2-(5-methyl-1-methylene-hex-4-enyl)-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one (27b), 8,8-Dimethyl-4-(4-methyl-pent-3-enyl)-5,7,8,9-tetrahydro-2*H*-benzo[*b*]-oxepin-6-one (28a), and 8,8-Dimethyl-3-(4-methyl-pent-3-enyl)-5,7,8,9-tetrahydro-2*H*-benzo[*b*]oxepin-6-one (28b): Treatment of **5** (166 mg, 1 mmol) with myrcene (2 mL) in the presence of $Rh_2(OPiv)_4$ (3 mg) afforded **27a** and **27b** (132 mg, 48%) as a 33:67 ratio of isomers and **28a** and **28b** (126 mg, 46%) as a 37:63 ratio as inseparable mixtures.

27a: Liquid. R_f = 0.43 (*n*-hexane/ethyl acetate, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08 (s, 6 H), 1.57 (s, 6 H), 1.92–2.05 (m, 4 H), 2.19 (s, 2 H), 2.27 (s, 2 H), 2.71 (s, 2 H), 5.03–5.19 (m, 3 H), 5.85 (dd, ^3J = 17.3, ^3J = 10.9 Hz, 1 H) ppm.

27b: Liquid. R_f = 0.43 (*n*-hexane/ethyl acetate, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (s, 6 H), 1.64 (s, 6 H), 2.20 (s, 2 H), 2.28 (s, 2 H), 2.57–2.67 (m, 1 H), 2.91–3.00 (m, 1 H), 4.90 (s, 1 H), 5.02 (s, 1 H), 5.13 (dd, ^3J = 5.1, ^3J = 1.1 Hz, 1 H), 5.15–5.22 (m, 1 H) ppm. IR (neat) of **27a** and **27b**: $\tilde{\nu}$ = 2961, 2930, 1638, 1404, 1221, 1169, 1144, 1047, 920 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{18}H_{26}O_2$ 274.1933; found 274.1932.

28a: Liquid. R_f = 0.63 (*n*-hexane/ethyl acetate, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99 (s, 6 H), 1.56 (s, 3 H), 1.57 (s, 3 H), 2.04–2.11 (m, 4 H), 2.16 (s, 2 H), 2.20 (s, 2 H), 3.25 (s, 2 H), 4.66 (d, ^3J = 6.4 Hz, 2 H), 5.03–5.06 (m, 1 H), 5.71 (t, ^3J = 6.4 Hz, 1 H) ppm.

28b: Liquid. R_f = 0.63 (*n*-hexane/ethyl acetate, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00 (s, 6 H), 1.64 (s, 3 H), 1.65 (s, 3 H), 2.04–2.11 (m, 4 H), 2.98 (s, 4 H), 3.16 (d, ^3J = 6.4 Hz, 2 H), 4.64 (s, 2 H), 5.06–5.03 (m, 1 H), 5.88 (t, ^3J = 6.4 Hz, 1 H) ppm. IR (neat) of **28a** and **28b**: $\tilde{\nu}$ = 2961, 2928, 1649, 1603, 1453, 1387, 1256, 1227, 1165, 1146, 1042, 976 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{18}H_{26}O_2$ 274.1933; found 274.1931.

6,6-Dimethyl-2-*cis*-propenyl-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one (29) and 2,8,8-Trimethyl-5,7,8,9-tetrahydro-2*H*-benzo[*b*]oxepin-6-one (30): Treatment of **5** (166 mg, 1 mmol) with *cis*-piperylene (2 mL) in the presence of $Rh_2(OPiv)_4$ (3 mg) afforded a mixture of **29** (82 mg, 40%) and **30** (105 mg, 51%) as a liquid.

29: R_f = 0.3 (*n*-hexane/ethyl acetate, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.07 (s, 3 H), 1.08 (s, 3 H), 1.72 (d, ^3J = 6.8 Hz, 3 H), 2.20 (s, 2 H), 2.26 (s, 2 H), 2.47–2.60 (m, 1 H), 2.95–3.08 (m, 1 H), 5.49–5.62 (m, 2 H), 5.64–5.77 (m, 1 H) ppm. IR (neat): $\tilde{\nu}$ = 2959, 2872, 1636, 1402, 1370, 1219, 1167, 1144, 1040, 918 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{13}H_{18}O_2$ 206.1307; found 206.1308.

30: R_f = 0.57 (*n*-hexane/ethyl acetate, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00 (s, 3 H), 1.02 (s, 3 H), 1.31 (d, ^3J = 6.5 Hz, 3 H), 2.17–2.46 (m, 2 H), 2.46–2.59 (m, 2 H), 3.16–3.35 (m, 2 H), 5.28–5.36 (m, 1 H), 5.64–5.72 (m, 1 H), 6.08–6.16 (m, 1 H) ppm. IR (neat): $\tilde{\nu}$ = 2959, 2872, 1678, 1647, 1605, 1372, 1263, 1223, 1165, 1040, 993, 906 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{13}H_{18}O_2$ 206.1307; found 206.1306.

2-(6,6-Dimethyl-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran-2-yl) Vinylacetate (31) and 8,8-Dimethyl-6-oxo-2,5,6,7,8,9-hexahydrobenzo-[*b*]oxepin-2-yl Acetate (32): Treatment of **5** (166 mg, 1 mmol) with 1-acetoxy-1,3-butadiene (2 mL) as a 1:1 mixture of *cis*- and *trans*-isomers in the presence of $Rh_2(OPiv)_4$ (3 mg) afforded **31** (143 mg, 40%) as a 23:77 mixture of *cis*- and *trans*-isomers and **32** (88 mg, 35%) as a liquid.

31: R_f = 0.47 (*n*-hexane/ethyl acetate, 1:1). *cis*-isomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.16 (s, 3 H), 2.20 (s, 2 H), 2.26 (s, 2 H), 2.54–2.62 (m, 1 H), 2.98–3.06 (m, 1 H), 5.06 (dd, ^3J = 8.7, ^3J = 6.6 Hz, 1 H), 5.66–5.75 (m, 1 H), 7.19 (d, ^3J = 6.6 Hz, 1 H) ppm. *trans*-isomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08 (s, 6 H), 2.13 (s, 3 H), 2.20 (s, 2 H), 2.26 (s, 2 H), 2.54–2.62 (m, 1 H), 2.98–3.06 (m, 1 H), 5.19–5.28 (m, 1 H), 5.51 (dd, ^3J = 12.3, ^3J = 8.5 Hz, 1 H), 7.40 (d, ^3J = 12.3 Hz, 1 H) ppm. IR (neat) of *cis*/*trans* isomers: $\tilde{\nu}$ = 2961, 2872, 1763, 1634, 1404, 1372, 1213, 1107, 1044, 939 916 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{14}H_{18}O_4$ 250.1205; found 250.1206.

32: R_f = 0.77 (*n*-hexane/ethyl acetate, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00 (s, 3 H), 1.02 (s, 3 H), 2.23 (s, 3 H), 2.19–2.38 (m, 4 H), 3.12–3.42 (m, 2 H), 5.76–5.81 (m, 1 H), 6.10–6.18 (m, 1 H), 6.82 (d, ^3J = 4.3 Hz, 1 H) ppm. IR (neat): $\tilde{\nu}$ = 2961, 2872, 1763, 1655, 1616, 1374, 1206, 1165, 1038, 974, 943 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{14}H_{18}O_4$ 250.1205; found 250.1202.

2-(1-Methylpropenyl)-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one (33) and 2,3-Dimethyl-5,7,8,9-tetrahydro-2*H*-benzo[*b*]oxepin-6-one (34): Treatment of **1** (138 mg, 1 mmol) with 3-methyl-1,3-pentadiene (2 mL) as a 1:1 mixture of *cis*- and *trans*-isomers in the presence of $Rh_2(OPiv)_4$ (3 mg) afforded **33** (159 mg, 83%) as a 44:55 mixture of isomers and **34** (31 mg, 16%) as a liquid.

33: R_f = 0.47 (*n*-hexane/ethyl acetate, 1:1). Major isomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.62 (s, 3 H), 1.63 (d, ^3J = 6.5 Hz, 3 H), 1.97–2.06 (m, 2 H), 2.31–2.36 (m, 2 H), 2.40–2.44 (m, 2 H), 2.53–2.66 (m, 1 H), 2.84–2.96 (m, 1 H), 5.41 (q, ^3J = 6.5 Hz, 1 H), 5.67 (dd, ^3J = 8.3, ^3J = 8.2 Hz, 1 H) ppm. Minor isomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.57 (s, 3 H), 1.66 (d, ^3J = 6.5 Hz, 3 H), 1.97–2.06 (m, 2 H), 2.31–2.36 (m, 2 H), 2.40–2.44 (m, 2 H), 2.53–2.66 (m, 1 H), 2.84–2.96 (m, 1 H), 5.13 (dd, ^3J = 8.2, ^3J = 8.1 Hz, 1 H), 5.57 (q, ^3J = 6.5 Hz, 1 H) ppm. IR (neat) of *cis*/*trans* isomers: $\tilde{\nu}$ = 2944, 2870, 1634, 1454, 1422, 1402, 1372, 1231, 1181, 1115, 1061, 1019, 930, 901 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{12}H_{16}O_2$ 192.1150; found 192.1148.

34: R_f = 0.67 (*n*-hexane/ethyl acetate, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (d, ^3J = 6.7 Hz, 3 H), 1.70 (s, 3 H), 1.78–1.87 (m, 2 H), 2.23–2.38 (m, 4 H), 3.00–3.24 (m, 2 H), 5.44 (q, ^3J = 6.7 Hz, 1 H), 5.83–5.88 (m, 1 H) ppm. IR (neat): $\tilde{\nu}$ = 2942, 1647, 1603, 1373, 1273, 1221, 1192, 1067, 1007, 845 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{12}H_{16}O_2$ 192.1150; found 192.1148.

2-Methyl-2-(2-methylpropenyl)-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one (35): Treatment of **1** (138 mg, 1 mmol) with 2,4-dimethyl-1,3-pentadiene (2 mL) in the presence of $Rh_2(OPiv)_4$ (3 mg) afforded **35** (194 mg, 94%) as a liquid. R_f = 0.5 (*n*-hexane/ethyl acetate, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.44 (s, 3 H), 1.65 (s, 3 H), 1.71 (s, 3 H), 1.97–2.06 (m, 2 H), 2.31–2.42 (m, 4 H), 2.72–2.89 (m, 2 H), 5.46 (s, 1 H) ppm. IR (neat): $\tilde{\nu}$ = 2959, 2872, 1634, 1453, 1404, 1368, 1219, 1167, 1144, 1100, 1042, 968, 916 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{13}H_{18}O_2$ 206.1307; found 206.1307.

2,6,6-Trimethyl-2-(2-methylpropenyl)-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one (36): Treatment of **5** (166 mg, 1 mmol) with 2,4-dimethyl-1,3-pentadiene (2 mL) in the presence of $Rh_2(OPiv)_4$ (3 mg) afforded **36** (218 mg, 93%) as a liquid. R_f = 0.4 (*n*-hexane/ethyl acetate, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.07 (s, 3 H), 1.09 (s, 3 H), 1.43 (s, 3 H), 1.64 (s, 3 H), 1.71 (s, 3 H), 2.21 (s, 2 H), 2.25 (s, 2 H), 2.72–2.89 (m, 2 H), 5.46 (s, 1 H) ppm. IR (neat): $\tilde{\nu}$ = 2963, 1634, 1402, 1273, 1242, 1167, 1146, 1067, 1028, 970, 912 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{15}H_{22}O_2$ 234.1620; found 234.1617.

9-Methyl-9-(2-methylpropenyl)-8,9-dihydrophenaleno[1,2-*b*]furan-7-one (37): Treatment of **7** (222 mg, 1 mmol) with 2,4-dimethyl-1,3-pentadiene (2 mL) in the presence of $Rh_2(OPiv)_4$ (3 mg) afforded **37** (281 mg, 97%) as a liquid. R_f = 0.34 (*n*-hexane/ethyl acetate, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.61 (s, 3 H), 1.75 (s, 6 H), 3.20 (q, ^2J = 15.0 Hz, 2 H), 5.61 (s, 1 H), 7.57 (t, ^3J = 8.1 Hz, 1 H), 7.69 (t, ^3J = 8.1 Hz, 1 H), 8.01–8.08 (m, 3 H), 8.58 (d, ^3J =

7.3 Hz, 1 H) ppm. IR (neat): ṽ = 2973, 2928, 1636, 1582, 1508, 1435, 1381, 1327, 1273, 1223, 1055, 1024, 891 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{20}H_{18}O_2$ 290.1307; found 290.1310.

3,4,5a,8,9,9a-Hexahydro-2*H*-dibenzofuran-1-one (38a), 3,4,5a,6,7,9a-Hexahydro-2*H*-dibenzofuran-1-one (38b), and 8-Oxatricyclo-[7.2.2.0^{2,7}]trideca-2(7),10-dien-3-one (39): Treatment of **1** (138 mg, 1 mmol) with 1,3-cyclohexadiene (2 mL) in the presence of $Rh_2(OAc)_{44}$ (4 mg) afforded **38a** and **38b** (80 mg, 42%) as a 51:49 mixture of isomers and **39** (76 mg, 40%) as a liquid.

38a: R_f = 0.5 (*n*-hexane/ethyl acetate, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.72–1.90 (m, 2 H), 1.93–2.12 (m, 4 H), 1.95–2.06 (m, 2 H), 2.29 (t, ^3J = 6.2 Hz, 2 H), 2.36 (t, ^3J = 6.0 Hz, 2 H), 3.07–3.16 (m, 1 H), 4.84 (dd, ^3J = 8.8, ^3J = 3.5 Hz, 1 H), 5.90–5.92 (m, 1 H), 6.14–6.19 (m, 1 H) ppm.

38b: R_f = 0.5 (*n*-hexane/ethyl acetate, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.72–1.90 (m, 2 H), 1.93–2.12 (m, 4 H), 1.95–2.06 (m, 2 H), 2.27 (t, ^3J = 6.2 Hz, 2 H), 2.36 (t, ^3J = 6.0 Hz, 2 H), 3.56 (d, ^3J = 8.6 Hz, 1 H), 4.94 (dt, ^3J = 8.6, ^3J = 3.5 Hz, 1 H), 5.74–5.77 (m, 1 H), 5.89–5.86 (m, 1 H) ppm. IR (neat) of **38a** and **38b**: ṽ = 3032, 1649, 1626, 1400, 1231, 1179, 1134, 1059, 999, 904 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{12}H_{14}O_2$ 190.0994; found 190.0990.

39: R_f = 0.67 (*n*-hexane/ethyl acetate, 1:1). M.p. 83 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.65–1.76 (m, 1 H), 1.80–1.90 (m, 3 H), 1.97–2.06 (m, 1 H), 2.13–2.29 (m, 2 H), 2.31 (t, ^3J = 6.3 Hz, 2 H), 2.37–2.48 (m, 1 H), 3.55–3.61 (m, 1 H), 4.65–4.69 (m, 1 H), 5.99 (dd, ^3J = 8.7, ^3J = 6.4 Hz, 1 H), 6.63 (dd, ^3J = 8.7, ^3J = 7.4 Hz, 1 H) ppm. IR (KBr): ṽ = 3042, 2944, 2866, 1645, 1595, 1456, 1431, 1379, 1281, 1182, 1136, 1065, 999, 982, 959 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{12}H_{14}O_2$ 190.0994; found 190.0998.

3,3-Dimethyl-3,4,5a,8,9,9a-hexahydro-2*H*-dibenzofuran-1-one (40a), 3,3-Dimethyl-3,4,5a,6,7,9a-hexahydro-2*H*-dibenzofuran-1-one (40b), and 5,5-Dimethyl-8-oxatricyclo[7.2.2.0^{2,7}]trideca-2(7),10-dien-3-one (41): Treatment of **5** (166 mg, 1 mmol) with 1,3-cyclohexadiene (2 mL) in the presence of $Rh_2(OPiv)_4$ (3 mg) afforded **40a** and **40b** (109 mg, 50%) as a 42:58 mixture of isomers and **41** (105 mg, 48%) as a liquid.

40a: R_f = 0.37 (*n*-hexane/ethyl acetate, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08 (s, 3 H), 1.09 (s, 3 H), 1.74–2.33 (m, 8 H), 3.11–3.19 (m, 1 H), 4.89 (d, ^3J = 8.6 Hz, 1 H), 5.92–5.95 (m, 1 H), 6.14–6.20 (m, 1 H) ppm.

40b: R_f = 0.37 (*n*-hexane/ethyl acetate, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (s, 3 H), 1.05 (s, 3 H), 1.74–2.33 (m, 8 H), 3.60 (d, ^3J = 8.6 Hz, 1 H), 4.96–5.01 (dt, ^3J = 8.6, ^3J = 4.0 Hz, 1 H), 5.77–5.80 (m, 1 H), 5.89–5.90 (m, 1 H) ppm. IR (neat) of **40a** and **40b**: ṽ = 3032, 2957, 1630, 1400, 1368, 1221, 1167, 1142, 1034, 1013, 916 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{14}H_{18}O_2$ 218.1307; found 218.1309.

41: R_f = 0.53 (*n*-hexane/ethyl acetate, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.97 (s, 3 H), 1.00 (s, 3 H), 1.56–1.78 (m, 1 H), 1.84–2.19 (m, 6 H), 2.36–2.46 (m, 1 H), 3.55–3.58 (m, 1 H), 4.65–4.69 (m, 1 H), 5.99 (dd, ^3J = 8.6, ^3J = 6.4 Hz, 1 H), 6.53 (dd, ^3J = 7.5, ^3J = 7.4 Hz, 1 H) ppm. IR (neat): ṽ = 3052, 2934, 2865, 1632, 1591, 1377, 1285, 1213, 1165, 1148, 1028, 986, 870 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{14}H_{18}O_2$ 218.1307; found 218.1308.

7b,8,9,11a-Tetrahydro-12-oxaindeno[2,1-*a*]phenalen-7-one (42a), 7b,10,11,11a-Tetrahydro-12-oxaindeno[2,1-*a*]phenalen-7-one (42b), and 43: Treatment of **7** (222 mg, 1 mmol) with 1,3-cyclohexadiene (2 mL) in the presence of $Rh_2(OPiv)_4$ (3 mg) afforded **42a** and **42b** (225 mg, 82%) as a 57:43 mixture of isomers and **43** (44 mg, 16%) as a liquid.

42a: R_f = 0.7 (*n*-hexane/ethyl acetate, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.90–2.36 (m, 4 H), 3.54–3.62 (m, 1 H), 5.19 (d, ^3J = 9.4 Hz, 1 H), 6.12–6.18 (m, 1 H), 6.24–6.31 (m, 1 H), 7.58 (t, ^3J = 7.4 Hz, 1 H), 7.71 (t, ^3J = 8.0 Hz, 1 H), 8.03 (d, ^3J = 7.0 Hz, 2 H), 8.09 (dd, ^3J = 8.0, ^4J = 1.1 Hz, 1 H), 8.59 (dd, ^3J = 7.4, ^4J = 1.2 Hz, 1 H) ppm.

42b: R_f = 0.7 (*n*-hexane/ethyl acetate, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.90–2.36 (m, 4 H), 4.03 (d, ^3J = 8.0 Hz, 1 H), 5.27 (dt, ^3J = 8.0, ^3J = 3.6 Hz, 1 H), 5.84–5.88 (m, 1 H), 6.07–6.20 (m, 1 H), 7.58 (t, ^3J = 7.4 Hz, 1 H), 7.70 (t, ^3J = 8.0 Hz, 1 H), 8.03 (d, ^3J = 7.0 Hz, 2 H), 8.08 (dd, ^3J = 8.0, ^4J = 1.1 Hz, 1 H), 8.58 (dd, ^3J = 7.4, ^4J = 1.2 Hz, 1 H) ppm. IR (neat) of **40a** and **40b**: ṽ = 3059, 2928, 1628, 1582, 1435, 1422, 1379, 1217, 1194, 1096, 1022, 864 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{19}H_{14}O_2$ 274.0994; found 274.0994.

43: R_f = 0.8 (*n*-hexane/ethyl acetate, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.86–2.10 (m, 2 H), 2.20–2.29 (m, 1 H), 2.56–2.66 (m, 1 H), 4.09–4.13 (m, 1 H), 5.0–5.02 (m, 1 H), 6.16 (dd, ^3J = 8.6, ^3J = 6.4 Hz, 1 H), 6.77 (dd, ^3J = 8.7, ^3J = 7.4 Hz, 1 H), 7.54 (t, ^3J = 7.4 Hz, 1 H), 7.66 (t, $_3J$ = 7.4 Hz, 1 H), 7.95 (dd, ^3J = 8.1, ^4J = 1.1 Hz, 1 H), 8.05 (dd, ^3J = 8.1, ^4J = 1.1 Hz, 1 H), 8.13 (dd, ^3J = 7.4, ^4J = 1.1 Hz, 1 H), 8.54 (dd, ^3J = 7.4, ^4J = 1.1 Hz, 1 H) ppm. IR (neat): ṽ = 3057, 2928, 1632, 1574, 1414, 1379, 1192, 1026, 902 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{19}H_{14}O_2$ 274.0994; found 274.0992.

2,3,4b,5,6,7,8,10a-Octahydro-1*H*-11-oxacycloocta[*a*]inden-4-one(44) and 2,3,4b,7,8,9,10,10a-Octahydro-1*H*-11-oxacycloocta[*a*]-inden-4-one (45): Treatment of **1** (138 mg, 1 mmol) with *cis*,*cis*-1,3-cyclooctadiene (2 mL) in the presence of $Rh_2(OPiv)_4$ (3 mg) afforded a mixture of **44** (118 mg, 54%) and **45** (35 mg, 16%) as a liquid.

44: R_f = 0.63 (*n*-hexane/ethyl acetate, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.40–1.52 (m, 3 H), 1.61–1.79 (m, 2 H), 1.95–2.11 (m, 4 H), 2.21–2.45 (m, 5 H), 3.25–3.35 (m, 1 H), 5.29 (dd, ^3J = 11.8, ^3J = 4.0 Hz, 1 H), 5.67 (dd, ^3J = 8.3, ^3J = 4.0 Hz, 1 H), 5.74–5.80 (m, 1 H) ppm. IR (neat): ṽ = 2928, 1632, 1454, 1393, 1242, 1182, 1086, 1059, 936 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{14}H_{18}O_2$ 218.1307; found 218.1310.

45: R_f = 0.5 (*n*-hexane/ethyl acetate, 1:1). M.p. 61–62 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33–1.41 (m, 2 H), 1.72–2.15 (m, 8 H), 2.33–2.44 (m, 4 H), 4.01 (t, ^3J = 8.0 Hz, 1 H), 4.58–4.66 (m, 1 H), 5.04 (dd, ^3J = 10.1, ^3J = 6.3 Hz, 1 H), 5.75–5.84 (m, 1 H) ppm. IR (KBr): ṽ = 3017, 2926, 2859, 1626, 1400, 1364, 1236, 1179, 1136, 1059, 1019, 987, 932, 912 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{14}H_{18}O_2$ 218.1307; found 218.1310.

2,2-Dimethyl-2,3,4b,5,6,7,8,10a-octahydro-1*H*-11-oxacycloocta[*a*]-inden-4-one (46) and 2,2-Dimethyl-2,3,4b,7,8,9,10,10a-octahydro-1*H*-11-oxacycloocta[*a*]inden-4-one (47): Treatment of **5** (166 mg, 1 mmol) with *cis*,*cis*-1,3-cyclooctadiene (2 mL) in the presence of $Rh_2(OPiv)_4$ (3 mg) afforded a mixture of **46** (143 mg, 58%) and **47** (37 mg, 15%) as a liquid.

46: R_f = 0.8 (*n*-hexane/ethyl acetate, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 (s, 3 H), 1.07 (s, 3 H), 1.37–1.80 (m, 5 H), 2.02–2.30 (m, 6 H), 2.33–2.41 (m, 1 H), 3.27–3.37 (m, 1 H), 5.28 (dd, ^3J = 11.8, ^3J = 4.0 Hz, 1 H), 5.69 (dd, ^3J = 10.1, ^3J = 4.0 Hz, 1 H), 5.73–5.80 (m, 1 H) ppm. IR (neat): ṽ = 2953, 2849, 1424, 1395, 1285, 1223, 1142, 1082, 1036, 943 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{16}H_{22}O_2$ 246.1620; found 246.1622.

47: R_f = 0.7 (*n*-hexane/ethyl acetate, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (s, 3 H), 1.10 (s, 3 H), 1.70–2.05 (m, 5 H), 2.08–2.35 (m, 7 H), 4.00 (t, ^3J = 7.0 Hz, 1 H), 4.58–4.66 (m, 1 H), 5.02 (dd, ^3J = 10.9, ^3J = 7.0 Hz, 1 H), 5.75–5.86 (m, 1 H) ppm. IR (neat): ṽ = 2932, 2870, 1651, 1454, 1404, 1370, 1053, 734 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{16}H_{22}O_2$ 246.1620; found 246.1619.

1-Isopropenyl-1-methylspiro[2.5]octan-4-one (49): Treatment of **48** (124 mg, 1 mmol) with 2,3-dimethyl-1,3-butadiene (2 mL) in the

presence of $Rh_2(OAc)_4$ (4 mg) afforded **49** (109 mg, 61%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.66 (d, ^2J = 4.6 Hz, 1 H), 1.05 (s, 3 H), 1.50 (d, ^2J = 4.6 Hz, 1 H), 1.56–1.76 (m, 5 H), 1.83 (s, 3 H), 1.98–2.21 (m, 2 H), 2.47–2.54 (m, 1 H), 4.74 (s, 1 H), 4.93 (s, 1 H) ppm. IR (neat): $\tilde{\nu}$ = 3083, 2938, 2865, 1694, 1642, 1447, 1377, 1362, 1316, 1285, 1184, 1134, 1080, 982, 891 cm^{-1}. HRMS: *m*/*z* [M$^+$] calcd. for $C_{12}H_{18}O$ 178.1358; found 178.1359.

Acknowledgments

This work was supported by a research grant from the Advanced Research Center at Yeungnam University (105096). Discussion of this work with Dr. Ronald Tepper is greatly appreciated.

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[11] After hydrogenation of **38a** and **38b**, a reduced product with a *cis* ring-junction was obtained: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.63 (dt, *J* = 8.0, 4.3 Hz, 1 H), 2.98 (dt, *J* = 8.0, 7.4 Hz, 1 H), 2.40 (t, *J* = 6.0 Hz, 2 H), 2.32 (t, *J* = 6.0 Hz, 2 H), 2.07–1.87 (m, 4 H), 1.81–1.62 (m, 4 H), 1.55–1.37 (m, 2 H) ppm. IR (neat): $\tilde{\nu}$ = 2940, 2865, 1626, 1402, 1275, 1231, 1181, 1125, 1059, 999, 932 cm^{-1}.

[12] Reaction of 1,3-cyclohexanedione with *cis*,*cis*-1,3-cyclooctadiene in the presence of 2 equiv. of CAN(IV) afforded *cis*-cycloadduct **44** (36%) and *trans*-cycloadduct (19%). *trans* adduct: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.89 (dd, *J* = 11.3, 6.4 Hz, 1 H), 5.66–5.57 (m, 1 H), 5.14 (dd, *J* = 11.8, 6.4 Hz, 1 H), 2.91–2.82 (m, 1 H), 2.81–2.74 (m, 1 H), 2.44–2.08 (m, 5 H), 2.04–1.88 (m, 3 H), 1.80–1.68 (m, 1 H), 1.63–1.49 (m, 2 H), 1.36–1.07 (m, 2 H) ppm. IR (neat): $\tilde{\nu}$ = 3032, 1649, 1626, 1402, 1229, 1179, 1134, 1059, 1001, 980, 959, 907 cm^{-1}.

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Received: June 30, 2004

