Ligand-Induced Selectivity in the Rhodium(II)-Catalyzed Reactions of α-Diazo Carbonyl Compounds†

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Received August 29, 1995⊗

3-Allyl-2,5-diazopentanedione and 3-butenyl-2,5-diazopentanedione were allowed to react with a trace amount of a rhodium(II) catalyst in methylene chloride at room temperature. The major products isolated correspond to the internal trapping of a carbonyl ylide as well as intramolecular cyclopropanation. Changing the catalyst from $Rh_2(OAc)_4$ to $Rh_2(cap)_4$ to $Rh_2(tfa)_4$ caused a significant alteration in product distribution. A rather unusual and unexpected regiochemical crossover in the cycloaddition occurred when $Rh_2(tfa)_4$ was used and is most likely due to complexation of the metal with the dipole. A computational approach to rationalize the observed product distribution was carried out. The thermodynamic stabilities of cycloaddition transition states were approximated from the computationally derived strain energies of ground state molecules using traditional force-field techniques. Globally minimized ground state energies were obtained for all possible cycloaddition products, and final strain energies were calculated. In all cases studied, the lower energy isomer corresponded to the cycloadduct actually isolated. A study of the regiochemical aspects of the Rh(II)-catalyzed reaction of 1-diazo-3-(2-oxo-2-phenylethyl)hexane-2,5-dione was also carried out. Cyclization of the initially formed rhodium carbenoid occurred exclusively across the acetyl rather than the benzoyl group. The structure of the internal cycloadduct was assigned on the basis of a proton-detected multiple-bond heteronuclear multiple-quantum coherence experiment.

Catalytic methods for the generation of metallocarbenes have attracted a great deal of attention in recent years.[1−6] Early work in this area made use of insoluble copper catalysts.[7] Although these catalysts are still employed today, their use has decreased significantly with the advent of homogeneous copper catalysts[8] and catalysts based on other metals.[9] The discovery that rhodium(II) carboxylates facilitate nitrogen loss from diazo compounds rekindled significant interest in the field of diazo-carbenoid chemistry.[10] Since the realization that Rh(II) carboxylates are superior catalysts for the generation of transient electrophilic metal carbenoids from α-diazo carbonyl compounds, intramolecular carbenoid addition reactions have assumed strategic importance in C−C bond-forming reactions in organic synthesis.[11] Metallocarbenoid reactions involving X−H insertion (X = C, O, N),[12] cyclopropanation,[13] or ylide generation[14] have also been used to prepare complex synthetic targets.

While many of the recent reports deal with controlling the stereoselectivity[1−4] and, in particular with chiral catalysts, the enantioselectivity of metal-catalyzed diazo carbonyl reactions,[15−19] there are a growing number of examples which also address the question of chemoselectivity.[9] Site selectivity has not only been found to depend on the type of α-diazo carbonyl utilized but is also governed by steric,[20−22] conformational,[23] and electronic factors.[24−27] The question of chemoselectivity of rhodium

† This paper is dedicated to Professor Peter Beak on the occasion of his 60th birthday.

⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1995.

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carbenoids has been probed by the preparation of diazo carbonyl compounds containing two different reaction sites and the study of the competition between the two carbenoid processes.[27] These studies have revealed some dramatic ligand effects; for example, carboxylate and carboxamide ligands in rhodium(II) catalysts can effectively control chemoselectivity in competitive carbenoid transformations of diazo carbonyl compounds. This powerful method of manipulation *has the potential to alter the chemoselectivity of gram quantities of reactant, by changing milligram quantities of the catalyst.* As a continuation of our studies in this area, we have found that, in certain cases, regiochemical control of the intramolecular cycloaddition process is also sensitive to the bridging ligands of the rhodium(II) catalyst.[28] In addition to ligand effects, the tether length of the pendant olefin also influences regiochemistry. The regiochemical outcome of the reaction was correlated with computationally determined strain energies of the resulting cycloadducts. The present paper documents the results of these studies.

Results and Discussion

Our own interest in transition metal carbene-mediated processes has centered on ylide formation,[29] intramolecular cyclopropanation,[27a] and X−H insertion reactions,[30] and we have recently described the results of experiments designed to probe their efficiency as a function of the nature of the catalyst.[27] We previously reported[27] that the rhodium(II) acetate-catalyzed decomposition of 3-allyl-1-diazo-2,5-pentanedione (**1**) provides two products: the carbonyl derived cycloadduct **3** and the cyclopropanated product **4a** (*trans*). A more detailed analysis showed

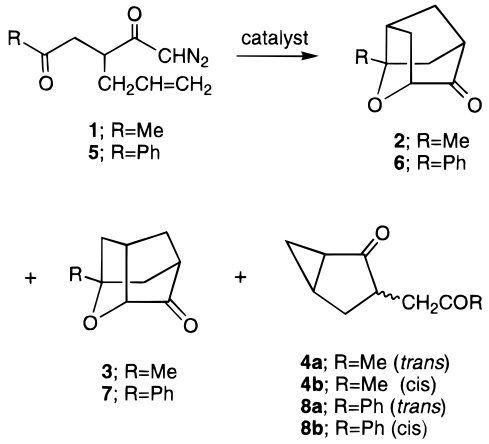

Table 1. Competition between Carbonyl Ylide Formation and Cyclopropanation in Rh_2L_4-Catalyzed Reactions of α-Diazo Ketones 1 and 5

diazo ketone	Rh_2L_4	isolated yield, %	relative yield, %			
			2	**3**	**4a**	**4b**
1	$Rh_2(OAc)_4$	83	6	41	22	14
1	$Rh_2(cap)_4$	82	8	25	34	15
1	$Rh_2(pfb)_4$	58	0	18	27	13
1	$Rh_2(tfa)_4$	71	0	35	24	12
1	$Cu(acac)_2$	94	0	9	75	10
1	$PdCl_2(PhCN)_2$	89	0	0	83	6
diazo ketone	Rh_2L_4	isolated yield, %	relative yield, %			
			6	**7**	**8a**	**8b**
5	$Rh_2(OAc)_4$	94	10	47	23	14
5	$Rh_2(cap)_4$	96	12	52	28	4
5	$Rh_2(pfb)_4$	87	33	12	25	17
5	$Rh_2(tfa)_4$	93	34	12	17	30
5	$Cu(acac)_2$	98	9	35	34	20
5	$PdCl_2(PhCN)_2$	68	0	0	38	30

that the reaction of **1** was more complicated than originally reported. Thus, addition of α-diazo ketone **1** to a mixture of the catalyst in CH_2Cl_2 at 25 °C resulted in the formation of four different compounds which were eventually separated by silica gel chromatography and identified as compounds **2**−**4**. The major product isolated (**3**; 41%) corresponded to the internal trapping of a carbonyl ylide intermediate. The product distribution was also examined as a function of the transition metal catalyst used, and the results of this study are collected in Table 1. A study of the closely related allyl-1-diazo-5-phenyl-2,5-pentanedione (**5**) was also carried out using a similar set of catalysts (Table 1). Once again, the major product corresponded to the internal trapping of a carbonyl ylide. Using rhodium(II) acetate or caprolactamate [$Rh_2(cap)_4$], the ratio of internal cycloadducts (**6**:**7**) remained unchanged. Changing the catalyst to rhodium(II) trifluoroacetate [$Rh_2(tfa)_4$] or rhodium(II) perfluorobutyrate [$Rh_2(pfb)_4$], however, caused a significant alteration in product distribution. Cycloadduct **6** was the major product isolated with the fluorinated ligands, whereas cycloadduct **7** was the major regioisomer formed with the other two catalysts. Intramolecular cyclopropanation occurs to a considerable extent with all the rhodium(II) catalysts and is significantly enhanced using $Cu(acac)_2$ or $PdCl_2(PhCN)_2$ (see Table 1).

The effect of elongating the tether length was probed by studying the transition metal catalyzed decomposition of 3-(3-butenyl)-1-diazo-5-phenyl-2,5-pentanedione (**9**). When $Rh_2(OAc)_4$ was used as the catalyst, the two cycloaddition regioisomers **10** (65%) and **11** (9%) were formed together with lesser quantities (11%) of a *cis*/*trans* mixture of bicyclo[4.1.0]heptane **12**. Little difference in the cycloadduct distribution was encountered with all the rhodium(II) catalysts studied. It should also be noted that the intramolecular cyclopropanation pathway with this system is significantly diminished relative to α-diazo ketone **5**, and this is presumably related to conformation/entropic factors.

Decomposition of the isomeric 4-alkenyl-2,5-diazopentanediones **13** and **20** also occurred readily in the presence of a catalytic amount of rhodium(II) acetate to give a single [3 + 2] cycloadduct (*i.e.*, **14**) as well as the product derived from cyclopropanation (**15**). Yields for cyclopropanation are lower than those for cycloaddition, irrespective of the nature of the ligand (Table 2). When $PdCl_2(PhCN)_2$ was used as the catalyst, only the cyclopropanated product **15** (assumed *trans*) was obtained but

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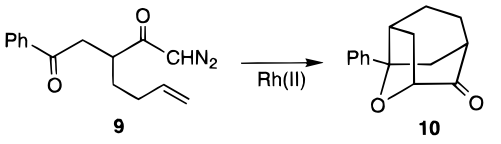
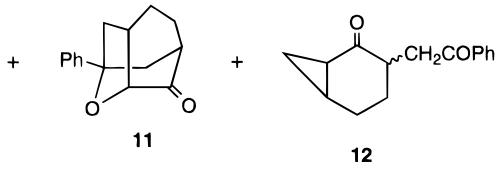
Table 2. Competition between Carbonyl Ylide Formation and Cyclopropanation in Rh_2L_4-Catalyzed Reactions of α-Diazo Ketone 13

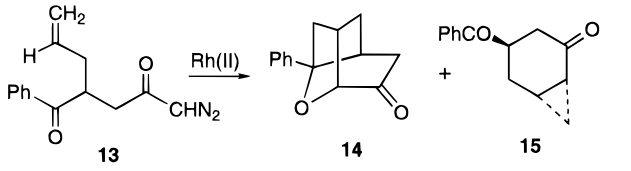
diazo ketone	Rh_2L_4	isolated yield, %	relative yield, %		
			14	**15**	**18**
13	$Rh_2(OAc)_4$	70	40	30	0
13	$Rh_2(cap)_4$	99	55	44	0
13	$Rh_2(pfb)_4$	59	0	20	39
13	$Rh_2(tfa)_4$	85	0	35	50
13	$Cu(acac)_2$	94	52	42	0
13	$PdCl_2(PhCN)_2$	46	0	46	0

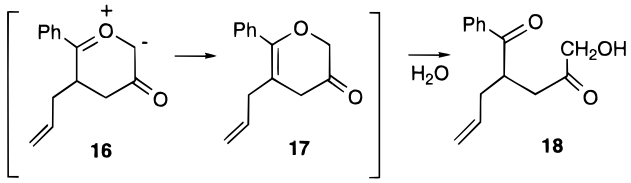
in significantly lower yield (Table 2). With $Rh_2(pfb)_4$ or $Rh_2(tfa)_4$ as the catalyst, none of the internal cycloadduct





14 was obtained. Instead, a mixture of **15** and hydroxyketone **18** (40−50%) was formed. More than likely the formation of **18** involves a 1,4-hydrogen shift of the initially generated carbonyl ylide **16** to give enol ether





17 which undergoes a subsequent hydrolysis on workup. Deuterium-labeling studies by Landgrebe[31] have provided strong evidence that the hydrogen shift observed in carbonyl ylides is an intramolecular process. Interestingly, the bimolecular reaction of **13** with benzene occurs to give **19** to the exclusion of carbonyl ylide generation or cyclopropanation with the carbenoid generated with $Rh_2(tfa)_4$ or $Rh_2(pfb)_4$. Clearly there are major differences in the behavior of the carbonyl ylide when fluorinated ligands of Rh(II) are used. What is so remarkable about this result is the degree to which chemoselectivity can be achieved over such a broad spectrum of carbene transformations by simply changing the dirhodium(II) ligand from acetate to a trifluoroacetate group.

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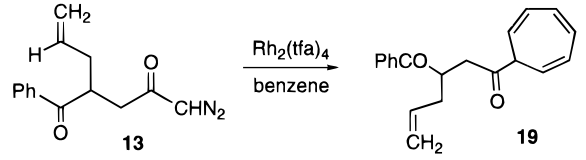
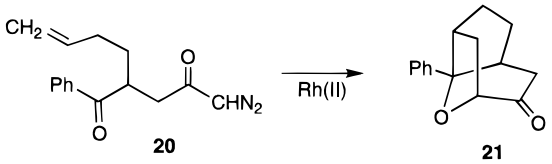
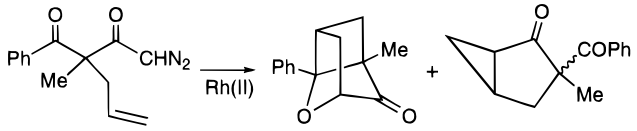


The exclusive formation of the intramolecular [3 + 2] cycloadduct **21** from the reaction of 4-butenyl-2,5-diazopentanedione **20** with $Rh_2(OAc)_4$ (82%), $Rh_2(tfa)_4$ (78%), and $Rh_2(cap)_4$ (66%) is worth noting since it represents a regiochemical crossover in the cycloaddition of the alkene with the dipole. In the previous example (**13** → **14**), the alkenyl group approached the dipole from the side opposite to its own attachment, whereas with **20** the approach was from the same side of attachment. This crossover suggests that electronic, steric, and conformational factors all play an important role in the control of regiochemistry. The structure of cycloadduct **21** was unequivocally established by an X-ray crystal analysis of its corresponding *N*,*N*-diphenylhydrazone derivative. [32]



The effect that a variation in the spatial proximity between the carbonyl group and the α-diazo ketone would have on the course of the reaction was studied by diminishing the length of the methylene tether separating the two functionalities. The majority of systems examined in the literature involve the formation of six-membered-ring carbonyl ylide intermediates.[4,14] Systems that are separated by a single methylene group should form five-membered-ring ylides. If the α-position of the 5-ring carbonyl ylide dipole contains a hydrogen atom, proton transfer is known to proceed at a faster rate than dipolar cycloaddition.[33] To avoid this complication, we examined the Rh(II)-catalyzed reaction of α-diazo ketone **22**. Reaction of **22** with $Rh_2(OAc)_4$ in CH_2Cl_2 afforded a 5:2-mixture of the internal cycloaddition product **23** and the cyclopropanated products **24**. Catalysis by $Rh_2(tfa)_4$, on the other hand, resulted in the exclusive formation of the internal cycloadduct **23**. The structure of **23** was unequivocally established by an X-ray analysis of its *N*,*N*-diphenylhydrazone derivative.



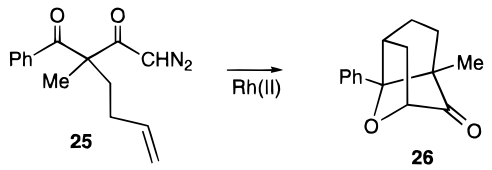
$Rh_2(OAc)_4$	60%	24%
$Rh_2(tfa)_4$	67%	0%
$Rh_2(cap)_4$	70%	28%

A similar tandem cyclization−ycloaddition sequence also occurred with the homologous butenyl-substituted α-diazo ketone **25**. The only product formed with this

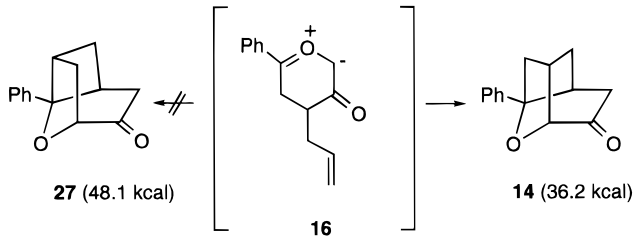
(32) The authors have deposited coordinates for the *N*,*N*-diphenylhydrazone derivatives of structures **21** and **23** with the Cambridge Data Centre. The coordinates can be obtained from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

(33) Padwa, A.; Chinn, R. L.; Hornbuckle, S. F.; Zhang, Z. J. *J. Org. Chem.* **1991**, *56*, 3271.

system (>95% yield) corresponded to cycloadduct **26**. In this case, replacement of the acetate ligand with perfluorobutyrate or caprolactam did not alter the course of the reaction. This apparent selectivity is most likely related to the preference of metallocarbenoids to favor reaction with substrates located five-atoms away. Cyclopropanation would require reaction across a 6,7 π-bond and is entropically less favored than formation of the 5-ring carbonyl ylide.



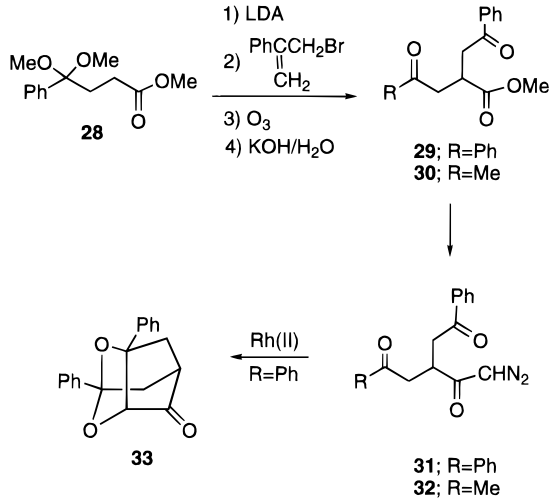
The observed crossover in regiochemical preference in the Rh(II)-catalyzed decomposition of diazo ketones **13** *vs* **20** implies a significant difference in the transition state for the intramolecular carbonyl ylide cycloaddition reaction. A computational approach to rationalize the observed product distribution was initiated. Molecular mechanics calculations represent a reliable, fast, and efficient way of determining molecular properties.[34] The thermodynamic stabilities of cycloaddition transition states can be approximated from the computationally derived strain energies of ground state molecules using traditional force-field techniques. Globally minimized ground state energies were obtained for all possible cycloaddition products using Bakmdl,[35] a Monte Carlo statistical search method, and final strain energies were subsequently calculated using the MMX force field.[36] In the 3-substituted 2,5-diazopentanedione system where both regioisomeric cycloadducts are observed, the MMX strain energy difference was calculated to be 0.6 kcal/mol for cycloadducts **6** and **7** and 0.7 kcal/mol for **10** and **11**. In systems where only one regioisomer was formed, substantial energy differences were noted. The difference in strain energy for cycloadduct **14** relative to the alternative regioisomer **27** was calculated to be 11.9 kcal/mol. The source for this large difference in strain energy is undoubtedly related to the presence of a cyclobutane ring in the skeleton of **27**. Cycloadducts **21**[18] and **26** were determined to be 4.3, 3.5, and 7.1 kcal/mol more stable than the alternative regioisomers. Thus, in all the cases studied, the lower energy isomer corresponded to the cycloadduct actually isolated. This is a subtle effect



which is not immediately obvious on inspection of molecular models but for which molecular mechanics calculations serve well to predict regiochemistry in such intramolecular dipolar cycloadditions.

The fact that the regiochemical distribution with diazo dione **5** is influenced by the nature of the rhodium ligand is most remarkable. Regiochemical control in [3 + 2] dipolar cycloaddition reactions has generally been rationalized on the basis of FMO considerations.[37] For carbonyl ylides, the HOMO of the dipole is dominant for reactions with electron-deficient dipolarophiles, while the LUMO becomes important for cycloaddition to more electron-rich species.[38] Cyclization of the lone pair of electrons of the neighboring carbonyl group onto the reactive α-ketometallocarbene intermediate is believed to be followed by dissociation of the catalyst and generation of a nonmetal complexed dipole.[14] However, the results encountered with diazo dione **5** require some mechanistic modification of this scheme. One possibility to account for this effect is that the dipole is not fully formed and the catalyst is bound to the original site of attachment. The resulting metal-complexed species could then undergo a subsequent intramolecular cycloaddition with a different regiochemical profile. This explanation is consistent with Davies recent observation of asymmetric cyclopropanation using α-hydroxy esters as chiral auxiliaries. [39]

All of the intramolecular tandem cyclization−cycloaddition reactions described so far involve systems possessing a tethered alkene as the internal dipolarophile. In an effort to increase the versatility of the process, we were led to examine the related cycloaddition using a tethered carbonyl group. Earlier studies in our laboratory had revealed that carbonyl ylides smoothly cycloadd across aldehydic π-bonds, and this type of cycloaddition was used in the total synthesis of brevicomin.[40] The dibenzoyl α-diazo keto system **31** was prepared in the straightforward manner illustrated below. The route features an LDA-induced allylation of methyl 4,4-dimethoxy-4-phenylbutyrate (**28**) with 3-bromo-2-phenyl-1-propene



followed by ozonization and hydrolysis to give carboxylic acid **29** which was readily converted to **31** in the standard

(34) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982.

(35) We gratefully acknowledge Professor Kosta Steliou of Boston University for a copy of the VMS Still−Steliou Model 2.96 program.

(36) Gajewski, J. J.; Gilbert, K. E.; McKelvey, J. *Advances in Molecular Modeling*; Liotta, D., Ed.; JAI Press: Greenwich, 1990; Vol. 2, p 65.

(37) Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley-Interscience: New York, 1984; Vol. I.

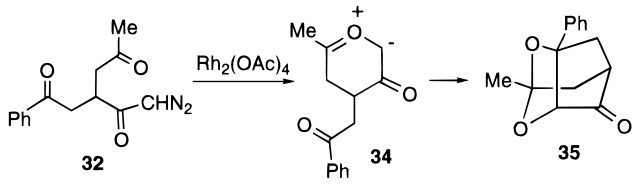
(38) Sustmann, R. *Tetrahedron Lett.* **1971**, 277. Sustmann, R.; Trill, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 838.

(39) Davies, H. M. L.; Cantrell, W. R., Jr. *Tetrahedron Lett.* **1991**, *32*, 6509. Davies, H. M. L.; Huby, N. J. S.; Cantrell, W. R., Jr.; Olive, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 9468.

(40) Padwa, A.; Fryxell, G. E.; Zhi, L. *J. Am. Chem. Soc.* **1990**, *112*, 3100. Padwa, A.; Chinn, R. L.; Zhi, L. *Tetrahedron Lett.* **1989**, *30*, 1491.

fashion. An analogous sequence of reactions was also used to prepare the related α-diazo ketone **32**. The Rh-(II)-catalyzed reaction of the symmetrical dibenzoyl system **31** gave cycloadduct **33** in 93% overall yield. The regiochemical outcome of the reaction is understandable on both electronic[40] and conformational bases.

Before describing the results of our investigations with the unsymmetrical α-diazo ketone **32**, it is worthwhile to comment on the spectroscopic method by which the structure (*i.e.*, **35**) of the resulting product was determined. The assignment was made on the basis of a proton-detected multiple-bond heteronuclear multiple-quantum coherence (HMBC) experiment.[41] This NMR experiment permits the identification of carbon−carbon connectivity through correlation between two- and three-bond $^1H-^{13}C$ coupling. A detailed analysis of the resonance assignments is given in the Experimental Section. Using the unsymmetrical α-diazo ketone **32**, the HMBC-NMR determination clearly established that dipole formation (*i.e.*, **34**) involved cyclization of the rhodium carbenoid with the acetyl group, and this was followed by a subsequent cycloaddition of **34** across the benzoyl π-bond to give **35** as the exclusive cycloadduct in 95% overall yield. No ligand effect was noted for this reaction.[42] It is tempting to speculate that the preferred cyclization of the acetyl group is related to its enhanced nucleophilicity relative to the benzoyl group.



In conclusion, several trends have surfaced from our investigations in this area. First and foremost, these studies have demonstrated that the intramolecular tandem cyclization−cycloaddition reaction of α-diazo ketones is a viable method for quickly assembling complex oxapolycyclic ring systems from easily prepared precursors. Both alkenes and tethered carbonyl groups readily undergo the cycloaddition. In certain cases, ligand substitution in the rhodium(II) catalyst can markedly alter the product ratio. With the perfluorinated ligands, the catalyst may still be coordinated with the dipole and this metal-complexed species could be involved in the cycloaddition. In general, the distribution of regioisomeric products from the internal cycloaddition appears to correlate well with product stabilities as determined by molecular mechanics calculations. We are continuing to explore the scope, generality, and synthetic applications of these Rh(II)-catalyzed reactions and will report additional findings at a later date.

Experimental Section

Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70 eV. Unless otherwise noted, all reactions were performed in oven-dried glassware under an atmosphere of dry nitrogen. Solutions were evaporated under reduced pressure with a rotary evaporator, and the residue was chromatographed on a silica gel column using an ethyl acetate−hexane mixture as the eluent unless specified otherwise.

General Procedure for the Rhodium(II)-Catalyzed Reaction of Alkenyl-Substituted 1-Diazoalkanediones. To a solution containing 0.20 mmol of the appropriate α-diazo ketone in 2 mL of benzene (or CH_2Cl_2) was added 2 mg of catalyst. The mixture was stirred under N_2 until TLC showed the absence of starting material. The solution was filtered, and the solvent was removed under reduced pressure. The crude product mixture was chromatographed on silica gel.

Preparation of 3-Allyl-1-diazo-2,5-hexanedione (1). A solution of LDA was prepared at −78 °C from 6.56 mL (46.7 mmol) of diisopropylamine in 60 mL of THF and 29.2 mL (46.7 mmol) of a 1.6 M *n*-butyllithium in hexane. After stirring at 0 °C for 1 h, the mixture was cooled to −78 °C and 8.0 g (45.9 mmol) of methyl 4-oxopentanoate ethylene ketal was added. The resulting solution was stirred at 25 °C for 5 h followed by cooling to −78 °C and the addition of 4.33 mL (50 mmol) of allyl bromide. After stirring at 25 °C for 24 h, the reaction was quenched with a saturated NH_4Cl solution. This solution was extracted with ether, and the ether layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel to give 7.99 g (82%) of methyl 2-allyl-4-oxopentanoate ethylene ketal as a pale yellow oil: IR (neat) 1738, 1642, 1437, 1377, and 1045 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.28 (s, 3H), 1.74 (dd, 1H, J = 14.4 and 2.4 Hz), 2.20 (dd, 1H, J = 14.4 and 10.4 Hz), 2.12−2.22 (m, 1H), 2.25−2.35 (m, 1H), 2.53−2.65 (m, 1H), 3.63 (s, 3H), 3.87−3.90 (m, 4H), 4.99−5.05 (m, 2H), and 5.66−5.80 (m, 1H).

A solution containing 7.15 g (33.4 mmol) of the above ketal and 2.77 g (11.1 mmol) of pyridinium *p*-toluenesulfonate in 300 mL of wet acetone was stirred at 80 °C for 12 h. After the solvent was removed under reduced pressure, the reaction mixture was diluted with ether, washed with a saturated $NaHCO_3$ solution, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the resulting residue was chromatographed on silica gel to give 5.62 g (99%) of methyl 2-allyl-4-oxopentanoate as a colorless oil: IR (neat) 1736, 1719, 1642, 1437, 1237, and 920 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.11 (s, 3H), 2.18−2.25 (m, 1H), 2.29−2.36 (m, 1H), 2.48 (dd, 1H, J = 17.4 and 4.0 Hz), 2.83 (dd, 1H, J = 17.4 and 9.1 Hz), 2.88−2.95 (m, 1H), 3.63 (s, 3H), 4.98−5.04 (m, 2H), and 5.59−5.71 (m, 1H).

A solution containing 2.0 g (11.8 mmol) of the above compound in 75 mL of THF was treated with 1.51 g (11.8 mmol) of potassium trimethylsilanolate. After the solution was stirred at 25 °C for 2 h, 1.5 mL (19.4 mmol) of methyl chloroformate was added. The reaction mixture was stirred for 4 h at rt and was then treated with 50 mmol of diazomethane in ether at 0 °C. The solution was allowed to warm to 25 °C over a 12 h interval. The solvent was removed under reduced pressure, and the resulting oil was chromatographed on silica gel to give 1.30 g (61%) of 3-allyl-1-diazo-2,5-hexanedione (**1**) as a yellow oil: IR (neat) 2105, 1717, 1638, 1327, and 920 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.10−2.19 (m, 1H), 2.14 (s, 3H), 2.31−2.41 (m, 1H), 2.46−2.52 (m, 1H), 2.80−3.03 (m, 2H), 5.05−5.10 (m, 2H), 5.37 (s, 1H), and 5.66−5.80 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.4, 35.8, 43.8, 44.1, 54.2, 117.0, 134.2, 196.0, and 206.3.

3-Methyl-2-oxatricyclo[3.3.1.0^{3,7}]nonan-9-one (2): IR (neat) 1762, 1449, 1381, 1261, 1080, and 801 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.30 (s, 3H), 1.70−1.73 (m, 2H), 1.85 (dt, 1H, J = 11.0 and 2.5 Hz), 1.91−1.94 (m, 1H), 1.92 (dd, 1H, J = 13.2 and 3.0 Hz), 2.24 (ddd, 1H, J = 13.2, 4.2, and 2.5 Hz), 2.42−2.49 (m, 1H), 2.97 (dd, 1H, J = 11.0 and 5.3 Hz), and 4.02 (dd, 1H, J = 5.3 and 1.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.2, 32.7, 37.2, 44.9, 45.9, 46.7, 79.6, 81.6, and 210.0. Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95, found C, 71.11; H, 7.86.

1-Methyl-2-oxatricyclo[3.3.1.0^{3,7}]nonan-4-one (3): IR (neat) 1734, 1549, 1449, 1348, 1034, and 833 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.55 (s, 3H), 1.76 (dd, 1H, J = 12.0 and 2.7 Hz), 1.85 (d, 1H, J = 11.7 Hz), 1.87 (dd, 1H, J = 11.7 and 3.1 Hz), 2.00−2.08 (m, 1H), 2.25 (dd, 1H, J = 11.4 and 5.2 Hz), 2.33 (dd, 1H, J = 11.4 and 2.7 Hz), 2.53 (t, 1H, J = 6.2

(41) Summers, M. F.; Marzilli, L. G.; Bax, A. *J. Am. Chem. Soc.* **1986**, *108*, 4285. Bax, A.; Summers, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 2093.

(42) Cycloadduct **35** was also obtained using the other Rh(II) carboxylates (*i.e.*, $Rh_2(cap)_4$, $Rh_2(tfa)_4$, and $Rh_2(pfb)_4$) in high yield.

Hz), 2.79−2.81 (m, 1H), and 4.19 (d, 1H, J = 4.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.1, 42.6, 42.8, 44.1, 49.4, 52.2, 84.1, 104.9, and 209.0. Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.97; H, 7.94.

***trans*-3-(2-Oxopropyl)bicyclo[3.1.0]hexan-2-one (4a):** IR (neat) 1715, 1364, 1213, and 922 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.61 (dd, 1H, J = 8.2 and 4.1 Hz), 1.05−1.13 (m, 1H), 1.37 (dd, 1H, J = 13.3 and 4.1 Hz), 1.67−1.75 (m, 1H), 1.78−1.87 (m, 1H), 1.96 (s, 3H), 2.25 (dd, 1H, J = 17.8 and 9.6 Hz), 2.34−2.46 (m, 1H), 2.50−2.62 (m, 1H), and 2.67 (dd, 1H, J = 17.8 and 3.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.0, 19.7, 27.9, 29.3, 29.5, 41.7, 46.3, 205.6, and 215.9. Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.93; H, 8.01.

***cis*-3-(2-Oxopropyl)bicyclo[3.1.0]hexan-2-one (4b):** IR (neat) 1715, 1365, 1211, 1161, and 824 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.00 (dd, 1H, J = 7.9 and 4.6 Hz), 1.12−1.22 (m, 1H), 1.61−1.76 (m, 2H), 1.87−1.98 (m, 1H), 2.10 (s, 3H), 2.23−2.36 (m, 2H), 2.41−2.49 (m, 1H), and 2.82 (dd, 1H, J = 17.9 and 4.3 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.3, 19.9, 28.2, 29.8, 36.2, 43.4, 46.6, 206.7, and 214.4. Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.95; H, 7.99.

Preparation of 3-Allyl-1-diazo-5-phenyl-2,5-pentanedione (5). To a 1 L round-bottom flask equipped with a Dean−Stark apparatus and a reflux condenser were added 30 g (156 mmol) of methyl 3-benzoylpropionate, 13.1 mL (234 mmol) of dry ethylene glycol, 500 mL of benzene, and a catalytic amount of *p*-toluenesulfonic acid. This mixture was heated at reflux until water formation had ceased. The resulting mixture was washed with a saturated $NaHCO_3$ solution and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the product was vacuum distilled to give 29.5 g (80%) of methyl 3-benzoylpropionate ethylene ketal as a colorless oil: IR (neat) 1740, 1437, 1169, and 702 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.22 (t, 2H, J = 6.8 Hz), 2.41 (t, 2H, J = 6.8 Hz), 3.62 (s, 3H), 3.72−3.77 (m, 2H), 3.97−4.01(m, 2H), 7.27−7.34 (m, 3H), and 7.41−7.45 (m, 2H).

A solution of lithium diisopropylamide was prepared in the standard manner from 6.36 mL (45.4 mmol) of diisopropylamine, and 7.15 g (30.3 mmol) of methyl 3-benzoylpropionate ethylene ketal was added at −78 °C. The resulting solution was stirred at 25 °C for 5 h followed by cooling to −78 °C and the addition of 5.54 mL (60.6 mmol) of allyl iodide. After the mixture was stirred at 25 °C for 24 h, the reaction was quenched with a saturated NH_4Cl solution. This solution was extracted with ether, and the ether layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel to give 7.01 g (84%) of methyl 2-allyl-3-benzoylpropionate ethylene ketal as a pale yellow oil: IR (neat) 1736, 1447, 1165, and 702 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.96 (dd, 1H, J = 14.5 and 2.7 Hz), 2.15−2.22 (m, 1H), 2.23−2.32 (m, 1H), 2.40 (dd, 1H, J = 14.5 and 10.4 Hz), 2.68−2.74 (m, 1H), 3.64 (s, 3H), 3.66−3.78 (m, 2H), 3.90−4.05 (m, 2H), 4.98−5.03 (m, 2H), 5.61−5.73 (m, 1H), 7.24−7.34 (m, 3H), and 7.41−7.45 (m, 2H).

A solution containing 6.00 g (21.7 mmol) of the above ketal and 1.80 g (7.24 mmol) of pyridinium *p*-toluenesulfonate in 300 mL of wet acetone was stirred at 80 °C for 12 h. After the solvent was removed under reduced pressure, the reaction mixture was diluted with ether, washed with a saturated $NaHCO_3$ solution, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the resulting residue was chromatographed on silica gel to give 4.58 g (91%) of methyl 2-allyl-3-benzoylpropionate as a colorless oil: IR (neat) 1736, 1688, 1217, and 756 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.31−2.41 (m, 1H), 2.45−2.54 (m, 1H), 3.06 (dd, 1H, J = 17.4 and 4.5 Hz), 3.11−3.16 (m, 1H), 3.44 (dd, 1H, J = 17.4 and 8.4 Hz), 3.68 (s, 3H), 5.05−5.11 (m, 2H), 5.68−5.82 (m, 1H), 7.44 (t, 2H, J = 7.4 Hz), 7.55 (t, 1H, J = 7.4 Hz), and 7.94 (d, 2H, J = 7.4 Hz).

A solution containing 4.0 g (17.2 mmol) of the above ester in 150 mL of THF was treated with 2.21 g (17.2 mmol) of potassium trimethylsilanolate. After the solution was stirred at 25 °C for 2 h, 2.0 mL (38.6 mmol) of methyl chloroformate was added. The reaction mixture was stirred for 4 h at rt and was then treated with 100 mmol of diazomethane in ether at 0 °C. The solution was allowed to warm to 25 °C over a 12 h interval. The solvent was removed under reduced pressure, and the resulting oil was chromatographed on silica gel to give 2.43 g (58%) of 3-allyl-1-diazo-5-phenyl-2,5-pentanedione (**5**) as a yellow oil: IR (neat) 2103, 1684, 1385, and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.20−2.30 (m, 1H), 2.40−2.49 (m, 1H), 3.02 (dd, 1H, J = 17.7 and 3.7 Hz), 3.03−3.19 (m, 1H), 3.54 (dd, 1H, J = 17.7 and 9.0 Hz), 5.07−5.13 (m, 2H), 5.43 (s, 1H), 5.65−5.83 (m, 1H), 7.46 (t, 2H, J = 7.4 Hz), 7.55 (t, 1H, J = 7.4 Hz), and 7.93 (d, 2H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 36.5, 40.0, 44.4, 55.1, 117.8, 128.0, 128.5, 133.2, 134.7, 136.5, 196.6, and 198.3.

3-Phenyl-2-oxatricyclo[3.3.1.0^{3,7}]nonan-9-one (6): mp 72−73 °C; IR (KBr) 1760, 1449, 1082, 754, and 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.76−1.80 (m, 1H), 1.89 (d, 1H, J = 12.5 Hz), 2.09−2.15 (m, 1H), 2.28 (dd, 1H, J = 13.2 and 3.0 Hz), 2.37 (d, 1H, J = 11.5 Hz), 2.45 (ddd, 1H, J = 13.2, 4.8, and 2.3 Hz), 2.58 (brs, 1H), 3.10 (dd, 1H, J = 11.5 and 5.5 Hz), 4.22 (dd, 1H, J = 5.5 and 1.5 Hz), and 7.23−7.39 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 32.7, 36.9, 45.3, 45.9, 47.3, 79.5, 84.8, 124.9, 127.4, 128.2, 141.1, and 209.3. Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.44; H, 6.59.

1-Phenyl-2-oxatricyclo[3.3.1.0^{3,7}]nonan-4-one (7): mp 83−84 °C; IR (KBr) 1735, 1451, 990, and 706 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.90 (dd, 1H, J = 11.9 and 2.8 Hz), 1.95 (d, 1H, J = 11.9 Hz), 2.19−2.26 (m, 1H), 2.27−2.34 (m, 1H), 2.37 (dd, 1H, J = 11.8 and 3.4 Hz), 2.56 (dd, 1H, J = 11.8 and 2.8 Hz), 2.88 (t, 1H, J = 6.1 Hz), 2.92−2.89 (m, 1H), 4.39 (d, 1H, J = 4.6 Hz), and 7.25−7.46 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 42.4, 42.8, 46.9, 49.8, 52.0, 84.0, 88.9, 125.0, 127.2, 128.1, 141.4, and 208.4. Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.42; H, 6.57.

***trans*-3-(2-Phenyl-2-ethyl)bicyclo[3.1.0]hexan-2-one (8a):** IR (neat) 1717, 1684, 1598, 1229, 1001, and 691 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.79 (dd, 1H, J = 8.2 and 4.2 Hz), 1.20−1.28 (m, 1H), 1.57 (dd, 1H, J = 13.5 and 3.6 Hz), 1.85−1.92 (m, 1H), 1.95−2.00 (m, 1H), 2.58−2.71 (m, 1H), 2.79−2.90 (m, 2H), 3.35−3.48 (m, 1H), 7.40 (t, 2H, J = 7.4 Hz), 7.51 (t, 1H, J = 7.4 Hz), and 7.86 (d, 2H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.4, 20.0, 28.3, 29.9, 42.0, 42.3, 127.9, 128.5, 133.2, 136.2, 197.3, and 216.6. Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.21; H, 6.66.

***cis*-3-(2-Phenyl-2-ethyl)bicyclo[3.1.0]hexan-2-one (8b):** IR (neat) 1723, 1001, and 691 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.10 (dd, 1H, J = 7.9 and 4.7 Hz), 1.23 (dd, 1H, J = 13.3 and 8.5 Hz), 1.74−1.82 (m, 1H), 1.83−1.90 (m, 1H), 2.01−2.09 (m, 1H), 2.47 (dd, 1H, J = 12.6 and 8.1 Hz), 2.70 (ddd, 1H, J = 17.5, 8.5, and 3.1 Hz), 2.86 (dd, 1H, J = 18.0 and 8.5 Hz), 3.51 (dd, 1H, J = 18.0 and 3.4 Hz), 7.44 (t, 2H, J = 7.4 Hz), 7.55 (t, 1H, J = 7.4 Hz), and 7.94 (d, 2H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.5, 20.1, 27.0, 30.4, 36.6, 39.0, 128.0, 128.6, 133.2, 136.6, 198.1, and 214.8. Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.32; H, 6.63.

Preparation of 3-(3-Butenyl)-1-diazo-5-phenyl-2,5-pentanedione (9). A solution of LDA was prepared in the normal manner from 11.37 mL (81.1 mmol) of diisopropylamine, and 12.78 g (54.1 mmol) of methyl 3-benzoylpropionate ethylene ketal was added at −78 °C. The resulting solution was stirred at 25 °C for 5 h followed by cooling to −78 °C and the addition of 19.7 g (108.2 mmol) of 4-iodobutene. After the mixture was stirred at reflux for 24 h, the reaction was quenched with a saturated NH_4Cl solution. This solution was extracted with ether, and the ether layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel to give 12.57 g (80%) of methyl 2-(3-butenyl)-3-benzoylpropionate ethylene ketal as a pale yellow oil: IR (neat) 1737, 1165, and 704 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.44−1.59 (m, 1H), 1.62−1.70 (m, 1H), 1.93 (dd, 1H, J = 14.5 and 2.6 Hz), 1.97−2.03 (m, 2H), 2.41 (dd, 1H, J = 14.5 and 10.5 Hz), 2.61−2.71 (m, 1H), 3.64 (s, 3H), 3.66−3.80 (m, 2H), 3.90−4.04 (m, 2H), 4.90−4.99 (m, 2H), 5.65−5.80 (m, 1H), 7.25−7.31 (m, 3H), and 7.41−7.45 (m, 2H).

A solution containing 3.61 g (12.4 mmol) of the above ketal and 2.06 g (8.1 mmol) of pyridinium *p*-toluenesulfonate in 150

mL of wet acetone was stirred at 80 °C for 12 h. After the solvent was removed under reduced pressure, the reaction mixture was diluted with ether, washed with a saturated $NaHCO_3$ solution, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the resulting residue was chromatographed on silica gel to give 2.68 g (89%) of methyl 2-(3-butenyl)-3-benzoylpropionate as a colorless oil: IR (neat) 1734, 1449, 1217, and 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.62−1.76 (m, 1H), 1.78−1.89 (m, 1H), 2.13 (q, 2H, J = 7.4 Hz), 3.04 (dd, 1H, J = 18.5 and 4.7 Hz), 3.07−3.15 (m, 1H), 3.47 (dd, 1H, J = 18.5 and 10.1 Hz), 3.70 (s, 3H) 4.97−5.08 (m, 2H), 5.74−5.88 (m, 1H), 7.45 (t, 2H, J = 7.3 Hz), 7.56 (t, 1H, J = 7.3 Hz), and 7.96 (d, 2H, J = 7.3 Hz).

A solution containing 1.90 g (7.71 mmol) of the above ester in 100 mL of THF was treated with 0.99 g (7.71 mmol) of potassium trimethylsilanolate. After the solution was stirred at 25 °C for 2 h, 0.90 mL (11.6 mmol) of methyl chloroformate was added. The reaction mixture was stirred for 4 h at rt and was then treated with 50 mmol of diazomethane in ether at 0 °C. The solution was allowed to warm to 25 °C over a 12 h interval. The solvent was removed under reduced pressure, and the resulting oil was chromatographed on silica gel to give 1.26 g (64%) of 3-(3-butenyl)-1-diazo-5-phenyl-2,5-pentanedione (**9**) as a yellow oil: IR (neat) 2103, 1686, 1351, and 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.38−1.47 (m, 1H), 1.62−1.69 (m, 1H), 1.97 (dd, 2H, J = 14.5 and 7.3 Hz), 2.85 (dd, 1H, J = 18.0 and 9.0 Hz), 2.83−2.99 (m, 1H), 3.40 (dd, 1H, J = 18.0 and 3.8 Hz), 4.83−4.93 (m, 2H), 5.39 (s, 1H), 5.51−5.73 (m, 1H), 7.26 (t, 2H, J = 7.3 Hz), 7.37 (t, 1H, J = 7.3 Hz), and 7.79 (d, 2H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 30.7, 37.2, 40.3, 43.9, 54.6, 114.9, 127.5, 128.1, 132.7, 136.0, 137.1, 196.8, and 197.6.

8-Phenyl-7-oxatricyclo[4.3.1.0^{3,8}]decan-10-one (10): mp 140−141 °C; IR (KBr) 1735, 1034, and 704 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.45−1.59 (m, 1H), 1.81 (ddd, 1H, J = 14.5, 7.7, and 3.3 Hz), 2.17−2.37 (m, 4H), 2.42−2.61 (m, 3H), 3.13 (dd, 1H, J = 9.2 and 8.6 Hz), 4.31 (dd, 1H, J = 8.2 and 1.7 Hz), and 7.23−7.45 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.1, 30.6, 40.4, 41.4, 42.0, 50.5, 82.6, 83.9, 124.5, 127.1, 128.2, 143.4, and 210.8. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.95; H, 7.01.

1-Phenyl-7-oxatricyclo[4.3.1.0^{3,8}]decan-9-one (11): mp 154−155 °C; IR (KBr) 1731, 1080, and 698 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.72 (dd, 1H, J = 7.5 and 3.5 Hz), 1.90 (dd, 1H, J = 8.2 and 3.5 Hz), 1.99−2.17 (m, 2H), 2.17−2.37 (m, 2H), 2.42−2.61 (m, 2H), 2.71 (dt, 1H, J = 8.5 and 2.0 Hz), 2.72 (dd, 1H, J = 9.9 and 2.0 Hz), 4.41 (d, 1H, J = 6.9 Hz), and 7.27−7.48 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.6, 22.9, 34.6, 39.0, 41.5, 41.9, 82.6, 83.3, 124.1, 127.2, 128.3, 144.4, and 211.3. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.89; H, 7.10.

***trans*-3-(2-Phenyl-2-ethyl)bicyclo[4.1.0]heptan-2-one (12):** IR (neat) 1717, 1221, and 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.18 (dd, 1H, J = 10.6 and 5.2 Hz), 1.24−1.32 (m, 1H), 1.59−1.66 (m, 1H), 1.72−1.83 (m, 2H), 1.84−1.93 (m, 2H), 2.05−2.17 (m, 1H), 2.70 (dd, 1H, J = 17.6 and 7.1 Hz), 2.87−2.98 (m, 1H), 3.55 (dd, 1H, J = 17.6 and 5.2 Hz), 7.43 (t, 2H, J = 7.4 Hz), 7.52 (t, 1H, J = 7.4 Hz), and 7.95 (d, 2H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.1, 21.2, 22.3, 25.8, 32.1, 38.7, 40.1, 128.0, 128.5, 133.0, 137.0, 198.6, and 210.4. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.91; H, 7.09.

Preparation of 1-Diazo-5-phenyl-4-(2-propenyl)-2,5-pentanedione (13). To a solution containing 6.7 g (42 mmol) of 1-phenyl-4-pentenone in 200 mL of THF was added 100 mL (50 mmol) of 0.5 M potassium bis(trimethylsilyl)amide at −78 °C. The solution was stirred for 0.5 h after which 6.9 mL (63 mmol) of ethyl 2-bromoacetate was added. The reaction mixture was allowed to warm to rt for 2 h and cooled to 0 °C, the reaction was quenched with 100 mL of 5% HCl, and the solution was extracted with ether. The organic extracts were treated with 100 mL of 10% KOH and 100 mL of methanol at rt for 2 h. The crude reaction mixture was washed with ether and acidified with 10% HCl. The solution was extracted with ether, washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give 6.9 g (75%) of 4-oxo-4-phenyl-3-(2-propenyl)butyric acid as a viscous yellow oil: IR (neat) 2981, 1702, 1603, and 1453 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.35 (dt, 1H, J = 14.5 and 7.5 Hz), 2.51 (dd, 1H, J = 12.1 and 6.0 Hz), 3.56 (dd, 1H, J = 17.3 and 4.8 Hz), 2.76 (dd, 1H, J = 17.3 and 9.5 Hz), 2.94−3.03 (m, 1H), 5.10−5.15 (m, 2H), 5.68−5.82 (m, 1H), 7.48 (t, 2H, J = 7.5 Hz), 7.60 (t, 1H, J = 7.5 Hz), 8.09 (d, 2H, J = 7.5 Hz), and 10.58 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 34.5, 35.5, 40.4, 118.4, 128.4, 129.1, 130.1, 133.8, 172.2, 178.3, and 180.4.

To a solution containing 1.5 g (7.0 mmol) of the above acid and 0.65 mL (8.5 mmol) of methyl chloroformate in 100 mL of ether was added 0.98 mL (7.0 mmol) of triethylamine. The resulting white suspension was stirred at rt for 1 h. The precipitated triethylamine hydrochloride was removed by filtration, and the resulting clear solution was immediately treated with 40 mmol of diazomethane at 0 °C. The mixture was allowed to warm to rt overnight, and the excess diazomethane was removed under reduced pressure. The resulting oil was chromatographed on silica gel to give 1.2 g (75%) of 1-diazo-5-phenyl-4-(2-propenyl)-2,5-pentanedione (**13**) as a bright yellow oil: IR (neat) 2105, 1739, and 1683 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.15−2.26 (m, 1H), 2.41−2.57 (m, 2H), 2.90−2.98 (m, 1H), 4.05−4.14 (m, 1H), 5.00−5.05 (m, 2H), 5.28 (s, 1H), 5.58−5.74 (m, 1H), and 7.42−7.57 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 32.1, 36.3, 41.6, 55.0, 117.8, 125.7, 128.4, 128.6, 133.1, 134.3, 193.2, and 202.1.

3,5-Methano-8-oxatricyclo-7-oxo-4-phenyl[3.2.1.0^{1,4}]-octane (14) was isolated as a clear oil: IR (neat) 2960, 1725, and 1127 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.41 (dt, 1H, J = 13.1 and 2.5 Hz), 2.27 (d, 1H, J = 13.1 Hz), 2.67−2.77 (m, 1H), 2.83 (dd, 1H, J = 16.4 and 1.6 Hz), 3.00−3.10 (m, 1H), 3.46 (dd, 1H, J = 16.4 and 6.2 Hz), 3.50−3.57 (m, 1H), 3.65−3.73 (m, 1H), 4.73 (d, 1H, J = 6.6 Hz), and 7.30−7.56 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 27.9, 37.0, 37.4, 39.2, 43.3, 84.5, 85.6, 124.6, 127.5, 128.4, 141.0, and 213.2; HRMS calcd for $C_{14}H_{14}O_2$ 214.0994, found 214.0994.

***trans*-4-Benzoylbicyclo[4.1.0]heptan-2-one (15)** was isolated as an oil: IR (neat) 2931, 1683, 1598, and 1580 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.06 (dd, 1H, J = 10.7 and 5.1 Hz), 1.35 (td, 1H, J = 9.0 and 5.1 Hz), 1.77−1.84 (m, 2H), 1.92 (dd, 1H, J = 13.0 and 12.0 Hz), 2.29−2.36 (m, 1H), 2.37−2.44 (m, 1H), 2.50 (dd, 1H, J = 15.0 and 13.0 Hz), 3.85−3.96 (m, 1H), and 7.26−7.93 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.1, 24.7, 26.7, 38.6, 45.7, 128.3, 128.7, 128.8, 133.5, 135.2, 199.7, and 209.1; HRMS calcd for $C_{14}H_{14}O_2$ 214.0994, found 214.0992.

1-Hydroxy-5-phenyl-4-(2-propenyl)-2,5-pentanedione (18) was isolated as a clear oil: IR (neat) 2954, 1737, and 1683 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.40 (m, 1H), 2.65 (ddd, 1H, J = 14.5, 7.5, and 7.0 Hz), 2.97 (dd, 1H, J = 13.2 and 7.5 Hz), 3.06 (dd, 1H, J = 17.0 and 4.8 Hz), 3.53 (dd, 1H, J = 17.0 and 9.3 Hz), 3.61 (s, 2H), 4.74−4.83 (m, 1H), 5.04−5.09 (m, 2H), 5.78−5.92 (m, 1H), 7.47 (t, 2H, J = 6.0 Hz), 7.56 (t, 1H, J = 6.0 Hz), and 7.98 (d, 2H, J = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 34.9, 36.4, 41.9, 51.7, 117.9, 128.4, 128.7, 133.1, 134.2, 137.8, 188.0, and 201.9; HRMS calcd for $C_{14}H_{16}O_3$ 232.1100, found 232.1104.

4-(2,4,6-Cycloheptatrienyl)-1-phenyl-2-(2-propenyl)-1,4-butanedione (19) was isolated (87%) as a clear viscous liquid when the reaction was carried out using benzene as the solvent: IR (neat) 2979, 1717, and 1681 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.14 (ddd, 1H, J = 14.6, 8.0, and 6.8 Hz), 2.38−2.46 (m, 2H), 2.69 (dd, 1H, J = 18.2 and 4.0 Hz), 3.24 (dd, 1H, J = 18.2 and 4.0 Hz), 4.01−4.08 (m, 1H), 4.97−5.08 (m, 4H), 5.59−5.73 (m, 1H), 6.22−6.29 (m, 2H), 6.53−6.55 (m, 2H), 7.43 (t, 2H, J = 7.5 Hz), 7.52 (t, 1H, J = 7.5 Hz), and 7.97 (d, 2H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 36.2, 40.9, 42.6, 47.9, 106.8, 107.1, 117.7, 126.0, 126.2, 128.4, 128.6, 129.7, 129.8, 132.9, 134.4, 136.3, 202.2, and 207.8; HRMS calcd for $C_{20}H_{20}O_2$ 292.1464, found 292.1465.

Preparation of 4-Benzoyl-1-diazo-2-oxo-7-octene (20). A solution of 75.8 mL (37.9 mmol) of 0.5 M potassium hexamethyldisilazide in toluene and 45 mL of THF was cooled to −78 °C, and 6.0 g (34.4 mmol) of 1-phenyl-5-hexen-1-one[43]

(43) Reissig, H.-U.; Hippeli, C. *Synthesis* **1991**, *56*, 3087.

was added. The solution was stirred at −78 °C for 1 h followed by the dropwise addition of 3.91 g (41.3 mmol) of methyl bromoacetate. After the mixture was stirred at −78 °C for 4 h, the reaction was quenched with 1 N HCl, and the solution was extracted with ether. The ether layer was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel to give 5.8 g (68%) of methyl 3-benzoyl-6-heptenoate as a pale yellow oil: IR (neat) 2952, 1738, 1449, 1206, and 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.50−1.59 (m, 1H), 1.71−1.83 (m, 1H), 2.02 (q, 2H, J = 7.2 Hz), 2.51 (dd, 1H, J = 16.8 and 4.8 Hz), 2.93 (dd, 1H, J = 16.8 and 9.2 Hz), 3.59 (s, 3H), 3.87−3.96 (m, 1H), 4.91−4.98 (m, 2H), 5.64−5.78 (m, 1H), 7.45 (t, 2H, J = 7.3 Hz), 7.54 (t, 1H, J = 7.3 Hz), and 7.97 (d, 2H, J = 7.3 Hz).

A solution containing 3.76 g (15.3 mmol) of the above ester in 75 mL of THF was treated with 2.94 g (22.9 mmol) of potassium trimethylsilanolate. After the solution was stirred at 25 °C for 2 h, 3.48 mL (45 mmol) of methyl chloroformate was added. The reaction mixture was stirred for 4 h at rt and was then treated with 144 mmol of diazomethane in ether at 0 °C. The solution was allowed to warm to 25 °C over a 12 h period. The solvent was removed under reduced pressure, and the resulting oil was chromatographed on silica gel to give 2.66 g (68%) of 4-benzoyl-1-diazo-2-oxo-7-octene (**20**) as a yellow oil: IR (neat) 2105, 1681, 1369, and 704 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.51−1.61 (m, 1H), 1.75−1.87 (m, 1H), 2.02 (q, 2H, J = 7.3 Hz), 2.50 (dd, 1H, J = 15.5 and 4.2 Hz), 2.94 (dd, 1H, J = 15.5 and 8.5 Hz), 4.05 (ddd, 1H, J = 11.4, 9.0, and 6.5 Hz), 4.91−4.93 (m, 1H), 4.97 (s, 1H), 5.28 (s, 1H), 5.65−5.76 (m, 1H), 7.45 (t, 2H, J = 7.3 Hz), 7.55 (t, 1H, J = 7.3 Hz), and 7.98 (d, 2H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.0, 31.4, 41.2, 42.0, 54.8, 115.5, 128.4, 128.6, 133.0, 136.5, 137.2, 192.9, and 202.8.

7-Phenyl-8-oxatricyclo[4.2.2.0^{3,7}]decan-9-one (21): IR (neat) 1731, 1044, and 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.42−1.50 (m, 2H), 1.56 (d, 1H, J = 11.1 Hz), 2.01−2.20 (m, 2H), 2.05 (d, 1H, J = 15.2 Hz), 2.47 (dd, 1H, J = 12.5 and 8.5 Hz), 2.53−2.57 (m, 1H), 2.78 (dt, 1H, J = 8.2 and 3.8 Hz), 2.84 (dd, 1H, J = 15.2 and 8.7 Hz), 4.48 (d, 1H, J = 8.5 Hz), and 7.23−7.45 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.4, 31.4, 38.2, 40.9, 41.4, 47.6, 81.8, 93.9, 124.6, 127.2, 128.4, 144.3, and 215.2. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.89; H, 7.06.

A solution containing 0.42 mmol of sodium ethoxide in 0.5 mL of ethanol was added slowly to a mixture of 95.5 mg (0.42 mmol) of **21** and 93 mg (0.42 mmol) of *N*,*N*-diphenylhydrazine hydrochloride in dry ethanol. The mixture stirred for 24 h, the insoluble material was filtered, and the filtrate was concentrated under reduced pressure. The residue was dissolved in 8 mL of CH_2Cl_2 and extracted with 0.1 N HCl followed by washing with Na_2CO_3. The ether layer was dried over Na_2SO_4 and filtered through a pad of silica to give 130 mg (79%) of 7-phenyl-8-oxatricyclo[4.2.2.0^{3,7}]decan-9-one diphenylhydrazone as a white solid: mp 155−156 °C; IR (neat) 1590, 1489, 1032, and 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.55−1.64 (m, 2H), 1.76 (dd, 1H, J = 12.4 and 1.0 Hz), 1.97−2.12 (m, 2H), 2.08 (d, 1H, J = 15.3 Hz), 2.47 (dd, 1H, J = 12.5 and 8.5 Hz), 2.53−2.57 (m, 2H), 2.78 (dt, 1H, J = 11.0 and 7.8 Hz), 5.08 (d, 1H, J = 7.7 Hz), and 7.03−7.45 (m, 15H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.8, 29.3, 31.2, 31.7, 39.9, 40.6, 47.7, 93.9, 121.2, 122.9, 123.3, 124.3, 124.6, 127.0, 128.2, 128.3, 129.0, 129.2, 129.4, 148.5, and 170.3. Details regarding the X-ray crystal structure are found in the supporting information.

Preparation of 3-Benzoyl-1-diazo-3-methyl-2-oxo-5-hexene (22). A solution of LDA was prepared in the normal manner from 13.51 mL (96.4 mmol) of diisopropylamine and 5.0 g (43.8 mmol) of 2-methyl-4-pentenoic acid at −78 °C. The resulting solution was heated to 50 °C for 1 h followed by cooling to −78 °C and the rapid addition of 5.22 mL (45.0 mmol) of benzoyl chloride. After the solution was stirred at −78 °C for 30 min, 16.2 mL (210 mmol) of methyl chloroformate was added and the reaction mixture was stirred for 6 h at rt. The mixture was concentrated to 50 mL, and 200 mL of ether was added. This solution was filtered, and the filtrate was cooled to 0 °C and then treated with 200 mmol of diazomethane in ether at 0 °C. The solution was allowed to warm to 25 °C over a 12 h period. The solvent was removed under reduced pressure, and the resulting oil was chromatographed on silica gel to give 5.21 g (49%) of 3-benzoyl-1-diazo-3-methyl-2-oxo-5-hexene (**22**) as a yellow oil: IR (neat) 2113, 1681, 1353, and 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.44 (s, 3H), 2.65 (dd, 1H, J = 14.4 and 7.4 Hz), 2.79 (dd, 1H, J = 14.4 and 7.4 Hz), 4.95−5.05 (m, 2H), 5.22 (s, 1H), 5.51−5.68 (m, 1H), 7.42 (t, 2H, J = 7.3 Hz), 7.51 (t, 1H, J = 7.3 Hz), and 7.82 (d, 2H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.5, 40.7, 54.8, 61.7, 119.2, 128.4, 128.9, 132.2, 132.8, 135.7, 193.7, and 198.7.

1-Methyl-7-phenyl-6-oxatricyclo[3.2.1.0^{3,7}]octan-8-one (23): IR (neat) 1760, 1698, and 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.79 (s, 3H), 1.62 (d, 1H, J = 11.1 Hz), 1.94 (d, 1H, J = 12.3 Hz), 2.10−2.16 (m, 2H), 3.04 (t, 1H, J = 6.7 Hz), 4.67 (d, 1H, J = 4.4 Hz), and 7.34−7.50 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.4, 35.9, 36.8, 39.0, 53.7, 80.1, 92.0, 125.1, 128.2, 128.5, 135.1, and 212.1. Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.38; H, 6.55.

A solution containing 1.21 mmol of sodium ethoxide in 3.0 mL ethanol was added slowly to a mixture of 260 mg (1.21 mmol) of **23** and 268 mg (1.21 mmol) of *N*,*N*-diphenylhydrazine hydrochloride in 3.0 mL of dry ethanol. The mixture was stirred for 24 h, the insoluble material that formed was filtered, and the filtrate was concentrated under reduced pressure. The residue was dissolved in 20 mL of CH_2Cl_2 and extracted with 0.1 N HCl followed by further washing with an aqueous Na_2CO_3 solution. The ether layer was dried over Na_2SO_4 and filtered through a pad of silica to give 322 mg (70%) of 1-methyl-7-phenyl-6-oxatricyclo[3.2.1.0^{3,7}]octan-8-one diphenylhydrazone as a white solid: mp 137−138 °C; IR (neat) 1596, 1493, 1015, and 702 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.03 (s, 3H), 1.16 (d, 1H, J = 12.0 Hz), 1.59 (d, 1H, J = 10.6 Hz), 1.58−1.69 (m, 1H), 2.12 (ddd, 1H, J = 10.6, 6.7, and 2.2 Hz), 2.81 (t, 1H, J = 6.7 Hz), 4.95 (d, 1H, J = 4.5 Hz), and 7.00−7.50 (m, 15H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.0, 35.9, 36.1, 38.6, 53.2, 75.6, 92.0, 119.4, 121.8, 123.5, 126.0, 126.2, 127.8, 128.4, 128.5, 128.9, 129.3, 135.7, 148.7, and 170.4. Details regarding the X-ray crystal structure are found in the supporting information.

***trans*-3-Benzoyl-3-methylbicyclo[3.1.0]hexan-2-one (24a):** IR (neat) 1723, 1679, 1268, and 698 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.24 (dd, 2H, J = 8.3 and 4.2 Hz), 1.44 (s, 3H), 1.99 (d, 1H, J = 14.3 Hz), 2.30 (ddd, 2H, J = 8.3, 4.2, and 3.0 Hz), 2.85 (dt, 1H, J = 14.3 and 3.0 Hz), 7.25 (t, 2H, J = 7.3 Hz), 7.50 (t, 1H, J = 7.3 Hz), and 7.84 (d, 2H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.4, 20.7, 24.4, 30.0, 36.5, 59.7, 128.4, 128.6, 132.5, 134.5, 198.2, and 213.4. Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.57; H, 6.62.

***cis*-3-Benzoyl-3-methylbicyclo[3.1.0]hexan-2-one (24b):** IR (neat) 1731, 1669, 1310, and 696 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.95 (dt, 1H, J = 5.0 and 4.0 Hz), 1.07 (dt, 1H, J = 7.5 and 6.3 Hz), 1.51 (s, 3H), 1.89 (ddd, 1H, J = 6.3, 5.1, and 4.0 Hz), 1.96 (ddt, 1H, J = 7.5, 5.1, and 5.0 Hz), 2.10 (dd, 1H, J = 13.2 and 5.0 Hz), 3.15 (d, 1H, J = 13.2 Hz), 7.38 (dd, 2H, J = 7.7 and 7.4 Hz), 7.47 (t, 1H, J = 7.4 Hz), and 7.92 (d, 2H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.1, 18.3, 24.6, 27.9, 36.0, 58.2, 128.2, 129.4, 132.6, 135.5, 199.6, and 211.2. Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.40; H, 6.56.

Preparation and Rhodium(II)-Catalyzed Reaction of 2-(3-Butenyl)-1-diazo-2-methyl-4-phenyl-2,4-butanedione (25). To a solution containing 2.9 g (20 mmol) of diisopropylamine in 25 mL of THF was added 12 mL (20 mmol) of a 1.6 M *n*-butyllithium solution dropwise at 0 °C, and the mixture was allowed to warm to rt for 30 min. The solution was then cooled to −78 °C, and 1.0 g (7.8 mmol) of 2-methyl-5-hexenoic acid[44] was added dropwise. The reaction mixture was allowed to warm to rt for 30 min, heated to 50 °C for 1 h, and then cooled to −78 °C, and 1.2 g (8.6 mmol) of benzoyl chloride was added. The solution was stirred at −78 °C for 1

(44) Jellal, A.; Santelli, M. *Tetrahedron Lett.* **1980**, *21*, 4487.

h after which 3.7 g (39 mmol) of methyl chloroformate was added and the solution warmed to rt overnight. The resulting suspension was filtered, treated with 100 mmol of diazomethane at 0 °C, and stirred for 6 h. The excess diazomethane was removed under reduced pressure, and the resulting yellow oil was chromatographed on a silica gel column to give 0.66 g (35%) of 2-(3-butenyl)-1-diazo-2-methyl-4-phenyl-2,4-butanedione (**25**) as a bright yellow oil: IR (neat) 2921, 2112, 1680, and 1634 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.19 (s, 3H), 1.78−2.07 (m, 4H), 4.82−4.92 (m, 2H), 5.21 (s, 1H), 5.61−5.70 (m, 1H), 7.32 (dd, 2H, J = 7.7 and 7.4 Hz), 7.43 (d, 1H, J = 7.4 Hz), and 7.77 (d, 2H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.4, 27.9, 29.6, 35.4, 54.7, 114.9, 128.5, 128.8, 132.8, 135.8, 137.7, 194.2, and 199.1.

To a solution containing 0.20 mmol of α-diazo ketone **25** in 2 mL of methylene chloride was added 2 mg of catalyst. The mixture was stirred under N_2 until TLC showed the absence of starting material. The solution was then filtered and the solvent removed under reduced pressure. The crude product mixture was chromatographed on silica gel to give 2,6-methano-3a-methyl-6a-phenyl-3,3a,4,5,6,6a-hexahydro-2*H*-cyclopenta[*b*]furan-3-one (**26**) as a yellow oil: IR (neat) 1696, 1605, and 995 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.75 (s, 3H), 1.34 (d, 1H, J = 13.2 Hz), 1.57−1.78 (m, 2H), 2.01 (ddd, 1H, J = 13.2, 9.3, and 5.1 Hz), 2.23−2.33 (m, 2H), 2.58 (dd, 1H, J = 9.3 and 9.0 Hz), 4.44 (d, 1H, J = 5.1 Hz), and 7.23−7.39 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.4, 29.4, 31.9, 37.1, 44.0, 58.0, 77.0, 98.0, 125.3, 127.6, 128.3, 138.0, and 217.1; HRMS calcd for $C_{15}H_{16}O_2$ 228.1151, found 228.1154.

Preparation of 1-Diazo-3-(2-oxo-2-phenylethyl)-5-phenylpentane-2,5-dione (31). To a solution containing 1.8 g (9.3 mmol) of methyl 4-oxo-4-phenylpropionate and 2.5 mL (23 mmol) of trimethyl orthoformate in 50 mL of methanol was added a catalytic amount of *p*-toluenesulfonic acid. The mixture was heated at 50 °C for 12 h, followed by the removal of methanol and methyl formate by distillation at 70 °C. The resulting oil was treated with 10 mg of sodium methoxide in 1 mL of methanol, washed with ether, dried over Na_2SO_4, and concentrated under reduced pressure. The crude solid that formed was recrystallized from ether/hexane to give 2.1 g (94%) of methyl 4,4-dimethoxy-4-phenylbutyrate (**28**) as a white crystalline solid: mp 34−35 °C; IR (neat) 1738, and 1445 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.94−2.00 (m, 2H), 2.17−2.22 (m, 2H), 3.10 (s, 6H), 3.48 (s, 3H), and 7.22−7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.6, 32.1, 48.5, 51.3, 102.7, 126.8, 127.7, 127.9, 139.8, and 173.2.

A solution of LDA was prepared at −78 °C from 1.2 mL (7.5 mmol) of diisopropylamine in 25 mL of THF and 4.3 mL (6.9 mmol) of 1.6 M *n*-butyllithium in hexane. After stirring at 0 °C for 1 h, the mixture was cooled to −78 °C and 1.5 g (6.2 mmol) of the above ketal was added. The resulting solution was stirred at 25 °C for 3 h followed by cooling to −78 °C and the addition of 3.6 mL (25 mmol) of 3-bromo-2-phenyl-1-propene.[45] After the mixture was stirred at 25 °C for 12 h, the reaction was quenched with a saturated NH_4Cl solution. This solution was extracted with ether, and the ether layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel to give 0.94 g (50%) of methyl 2-(2-oxo-2-phenylethyl)-4-phenylpent-4-enoate as a pale oil: IR (neat) 2944, 1733, and 1683 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.76 (dd, 1H, J = 13.9 and 8.0 Hz), 3.02−3.19 (m, 3H), 3.39 (dd, 1H, J = 17.2 and 8.3 Hz), 3.61 (s, 3H), 5.12 (s, 1H), 5.34 (s, 1H), and 7.23−7.90 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 37.5, 39.2, 39.4, 51.7, 115.1, 126.2, 127.7, 127.9, 128.4, 128.5, 133.1, 136.5, 140.0, 145.4, 175.2, and 197.9.

A stream of ozone was bubbled into a solution containing 0.90 g (2.9 mmol) of the above ester at −78 °C until a consistent blue color was obtained. An excess of methyl sulfide was added, and the mixture was stirred at rt for 18 h, followed by concentration under reduced pressure and silica gel chromatography to give 0.77 g (86%) of methyl 4-oxo-2-(2-oxo-2-phenylethyl)-4-phenylbutyrate as a clear oil: IR (neat) 2947, 1730, and 1681 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.34 (dd, 2H, J = 17.8 and 6.2 Hz), 3.55 (dd, 2H, J = 17.8 and 5.5 Hz), 3.60−3.66 (m, 1H), 3.66 (s, 3H), and 7.39−7.94 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 35.8, 39.4, 52.1, 128.0, 128.5, 133.2, 136.4, 174.7, and 197.7.

To a solution containing 0.57 g (1.8 mmol) of the above ester was added 0.20 g (3.7 mmol) of KOH in 15 mL of methanol and 15 mL of water. The mixture was stirred at rt for 1 h, followed by washing with ether and acidification to pH 2. The aqueous layer was extracted with ether, and the organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude acid was immediately treated with 0.11 mL (1.4 mmol) of methyl chloroformate in 10 mL of ether followed by the addition of 0.16 mL (1.2 mmol) of Et_3N. The resulting white suspension was stirred at rt for 1 h. The precipitated triethylamine hydrochloride was removed by filtration, and the solution was immediately treated with 20 mmol of diazomethane at 0 °C. The mixture was allowed to warm to rt overnight, and the excess diazomethane was removed under reduced pressure. The resulting oil was chromatographed on silica gel to give 0.15 g (30%) of 1-diazo-3-(2-oxo-2-phenylethyl)-5-phenylpentane-2,5-dione (**31**) as a bright yellow oil: IR (neat) 2103, 1680, and 1631 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.18 (dd, 2H, J = 17.9 and 5.5 Hz), 3.50 (dd, 2H, J = 17.9 and 7.9 Hz), 3.64−3.76 (m, 1H), 5.49 (s, 1H), and 7.37−7.90 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 40.0, 40.7, 55.5, 128.0, 128.6, 133.3, 136.3, 196.6, and 197.5.

Rhodium(II)-Catalyzed Reaction of 1-Diazo-3-(2-oxo-2-phenylethyl)-5-phenylpentane-2,5-dione (31). To a solution containing 0.20 mmol of α-diazo ketone **31** in 2 mL of CH_2Cl_2 was added 2 mg of catalyst. The mixture was stirred under N_2 until TLC showed the absence of starting material. Chromatography over silica gel gave 2,8-dioxa-1,7-diphenyltricyclo[3.3.1.$0^{3,7}$]nonan-4-one (**33**) in 93% yield as a clear oil: IR (neat) 2922, 1762, and 1680 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.27 (ddd, 1H, J = 13.1, 4.0, and 1.5 Hz), 2.51 (dd, 1H, J = 13.2 and 3.0 Hz), 2.61 (d, 1H, J = 13.1 Hz), 2.72 (ddd, 1H, J = 13.2, 2.8, and 1.5 Hz), 2.98−3.02 (m, 1H), 4.21 (d, 1H, J = 3.0 Hz), and 7.30−7.98 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 38.0, 44.6, 46.3, 83.6, 85.9, 109.5, 125.2, 125.4, 128.2, 128.3, 128.5, 129.2, 136.2, 139.2, and 206.3; HRMS calcd for $C_{19}H_{16}O_3$ 292.1100, found 292.1109.

Preparation of 1-Diazo-3-(2-oxo-2-phenylethyl)hexane-2,5-dione (32). A solution of LDA was prepared at −78 °C from 5.6 mL (34 mmol) of diisopropylamine in 50 mL of THF and 22 mL (34 mmol) of 1.6 M *n*-butyllithium in hexane. After stirring at 0 °C for 1 h, the mixture was cooled to −78 °C and 5.0 g (29 mmol) of methyl 4-oxopentanoate ethylene ketal was added. The resulting solution was stirred at 25 °C for 5 h followed by cooling to −78 °C and the addition of 6.3 mL (43 mmol) of 3-bromo-2-phenyl-1-propene.[45] After the mixture was stirred at 25 °C for 12 h, the reaction was quenched with a saturated NH_4Cl solution and extracted with ether. The ether layer was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The residue was chromatographed on a silica gel column to give 1.3 g (15%) of methyl 4-oxo-2-(2-phenyl-2-propenyl)pentanoate ethylene ketal as a clear oil: IR (neat) 3054, 2982, 1730, and 1436 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.19 (s, 3H), 1.78 (dd, 1H, J = 14.3 and 2.3 Hz), 2.18 (dd, 1H, J = 14.3 and 10.2 Hz), 2.57−2.65 (m, 2H), 2.75−2.79 (m, 1H), 3.55 (s, 3H), 3.77−3.89 (m, 4H), 5.07 (s, 1H), 5.26 (s, 1H), and 7.21−7.36 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.0, 31.7, 39.0, 39.8, 40.6, 51.2, 64.5, 108.9, 114.7, 126.2, 127.5, 128.2, 140.3, 145.6, and 176.1.

A stream of ozone was bubbled into a solution containing 1.0 g (3.4 mmol) of the above ester at −78 °C until a consistent blue color was obtained. An excess of methyl sulfide was then added, and the mixture was stirred at rt for 18 h. Concentration of the solution under reduced pressure followed by silica gel chromatography gave 0.64 g (64%) of methyl 4-oxo-2-(2-oxo-2-phenylethyl)pentanoate ethylene ketal as a light yellow oil: IR (neat) 2981, 1733, 1681, and 1210 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.26 (s, 3H), 1.84 (dd, 1H, J = 14.5 and 5.3 Hz), 2.14 (dd, 1H, J = 14.5 and 7.3 Hz), 3.11−3.20 (m, 2H), 3.34 (dd, 1H, J = 18.6 and 9.4 Hz), 3.59 (s, 3H), 3.83 (m, 4H), and 7.33−7.87 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.0,

(45) Hatch, L. F.; Patton, T. L. *J. Am. Chem. Soc.* **1954**, *76*, 2705.

36.1, 40.3, 41.0, 51.7, 64.4, 109.0, 127.9, 128.4, 133.0, 136.5, 175.9, and 197.8.

To a solution containing 0.17 g (0.58 mmol) of the above ester was added 0.4 g (0.7 mmol) of KOH in 10 mL of methanol and 8 mL of water. The mixture was stirred at rt for 3 h followed by washing with ether and acidification to pH 2. The aqueous layer was extracted with ether, and the organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude acid was immediately treated with 0.05 mL (0.70 mmol) of methyl chloroformate in 25 mL of ether followed by the addition of 0.08 mL (0.58 mmol) of Et_3N. The resulting white suspension was stirred at rt for 1 h, and the precipitated triethylamine hydrochloride was removed by filtration. The solution was treated with 10 mmol of diazomethane at 0 °C and was allowed to warm to rt overnight. The excess diazomethane was removed under reduced pressure, and the resulting oil was chromatographed on silica gel to give 0.05 g (36%) of 1-diazo-3-(2-oxo-2-phenylethyl)hexane-2,5-dione (**32**) as a bright yellow oil: IR (neat) 2100, 1712, and 1655 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.13 (s, 3H), 2.62 (dd, 1H, J = 18.1 and 5.3 Hz), 2.94 (dd, 1H, J = 18.1 and 8.0 Hz), 3.05 (dd, 1H, J = 17.7 and 5.5 Hz), 3.37 (dd, 1H, J = 17.7 and 7.6 Hz), 3.45−3.53 (m, 1H), 5.51 (s, 1H), and 7.38−7.91 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.9, 39.3, 40.4, 45.3, 64.4, 127.9, 128.6, 133.4, 136.2, 196.4, 197.4, and 206.1.

Rhodium(II)-Catalyzed Reaction of 1-Diazo-3-(2-oxo-2-phenylethyl)hexane-2,5-dione (32). To a solution containing 1.0 mmol of **32** in 5 mL of CH_2Cl_2 was added 2 mg of Rh(II) catalyst. The mixture was stirred under N_2 until TLC showed the absence of starting material. Chromatography over silica gel afforded 2,8-dioxa-1-methyl-7-phenyltricyclo-[3.3.1.$0^{3,7}$]nonan-4-one (**35**) as a light yellow oil in 95% yield when $Rh_2(OAc)_4$ was used as the catalyst: IR (neat) 2921, 1767, 1552, and 1337 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.58 (s, 3H), 2.15 (ddd, 1H, J = 13.2, 4.0, and 1.4 Hz), 2.22 (dd, 1H, J = 13.4 and 3.0 Hz), 2.33−2.38 (m, 1H), 2.44 (d, 1H, J = 13.2 Hz), 2.83−2.87 (m, 1H), 4.03 (d, 1H, J = 2.3 Hz), and 7.29−7.57 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.9, 37.9, 44.0, 45.8, 83.3, 85.6, 109.0, 125.1, 128.1, 128.5, 139.3, and 206.8; HRMS calcd for $C_{14}H_{14}O_3$ 230.0944, found 230.0945.

A proton-detected multiple-bond heteronuclear multiple-quantum coherence (HMBC) spectrum was obtained from data collected on a GN-600 Omega spectrometer at 25 °C. Operational frequencies used were 599.642 522 0 MHz for proton and 150.797 153 0 MHz for carbon. A 256 × 2048 data matrix was obtained with 128 scans per t_1 increment. A relaxation delay of 1200 ms was used and optimized in the first block for the signals of the $^1H-^{13}C$ coupled protons. Delays were set so that 10 Hz long-range couplings were emphasized. The ^{13}C 90° pulse width of 28 μs, and the corresponding power levels were computed from the sample. A 5747.13 Hz spectral window was implemented in the proton dimension (t_2), and a 35714.29 Hz window was used in the carbon dimension (t_1). The entire experiment was preceded by four dummy scans. The data were processed in magnitude mode with Felix software operating on an IBM RS6000 Model 320 workstation. A 90° phase-shifted squared sine bell filter was applied over the first 1024 data points in t_2, and a 45° phase-shifted squared sine bell filter was applied over the 256 points in the t_1 dimension. The second dimension was then zero filled to 2048 points prior to Fourier transformation. The resonance assignments for carbons C_3 and C_7 were verified using a DEPT NMR experiment, which showed that the resonance assigned to C_3 formed a bond with one hydrogen, while the resonance assigned to C_7 did not have any hydrogens attached to it. Carbon C_1 was identified on the basis of its chemical shift and also verified to be quarternary with the DEPT experiment. The HMBC two-dimensional spectrum showed a strong correlation between the protons on the methyl carbon and carbon C_1. Carbon C_7 showed a weaker correlation with the ortho phenyl protons (H_o). This is consistent with the reported observation that three-bond J_{CH} correlations are weaker than two-bond J_{CH} correlations.[41] Additional correlations were consistent with the assigned structure.

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health (CA-26751). Use of the high-field NMR spectrometer used in these studies was made possible through equipment grants from the NIH and NSF.

Supporting Information Available: ^1H NMR and ^{13}C NMR spectra for all compounds with high-resolution mass spectra and ORTEP drawings of **21** and **23** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO951576N