Cyclization−Cycloaddition Cascade of Rhodium Carbenoids Using Different Carbonyl Groups. Highlighting the Position of Interaction

Albert Padwa,* Zhijia J. Zhang, and Lin Zhi

Department of Chemistry, Emory University, Atlanta, Georgia 30322

chemap@emory.edu

Received March 15, 2000

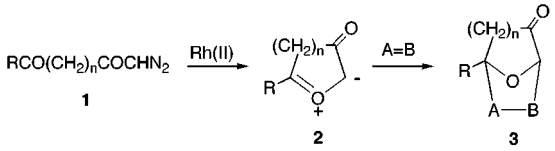
A series of 3-diazoalkanediones, when treated with a catalytic quantity of a rhodium(II) carboxylate, were found to afford oxabicyclic dipolar cycloadducts derived by the trapping of a carbonyl ylide intermediate. The reaction involves generation of the 1,3-dipole by intramolecular cyclization of the keto carbenoid onto the oxygen atom of the neighboring keto group. Both five- and six-ring carbonyl ylides are formed with the same efficiency. A study of the tandem cyclization−cycloaddition cascade of several α-diazo ketoesters was also carried out, and the cascade sequence proceeded in high yield. When the interacting keto carbonyl group was replaced by an imido group, the rhodium(II)-catalyzed reaction proceeded uneventfully. In contrast, α-diazo amidoesters do not undergo nitrogen extrusion on treatment with a Rh(II) catalyst. Instead, the diazo portion of the molecule undergoes 1,3-dipolar cycloaddition with various dipolarophiles to give substituted pyrazoles as the final products.

The role of α-diazo carbonyl compounds in organic synthesis is well established,[1−14] and in recent years much effort has been devoted to the study of the effect of different transition-metal catalysts on these reactions.[15−20] In earlier papers we described the formation of bridged oxabicycloalkanes from the rhodium(II)-catalyzed reaction of 1-diazoalkanediones.[21] The reaction involves the formation of a rhodium carbenoid intermediate and subsequent transannular cyclization of the electrophilic carbon onto the adjacent keto group to generate a cyclic carbonyl ylide, followed by 1,3-dipolar cycloaddition (Scheme 1).[22]

The primary spatial requirement for carbonyl ylide formation is that the distance between the two reacting centers should be sufficiently close so that effective overlap of the lone pair of electrons of the carbonyl group with the metallocarbenoid can occur. Most of the studies carried out involved five- and six-membered ring formation.[21] The resulting cyclic dipole (i.e., **2**) always contained a carbonyl group within the ring. All of our attempts to form carbonyl ylides from metal carbenoids that do not possess an adjacent carbonyl group failed to produce the dipole.[23] We assumed that, by increasing the electrophilic nature of the carbenoid intermediate, attack by the lone pair of electrons on the tethered carbonyl group is facilitated relative to other competitive pathways.

We[24] and others[25] have found that the intramolecular trapping of carbonyl ylide dipoles with tethered alkenes represents an effective method for the synthesis of a

Scheme 1



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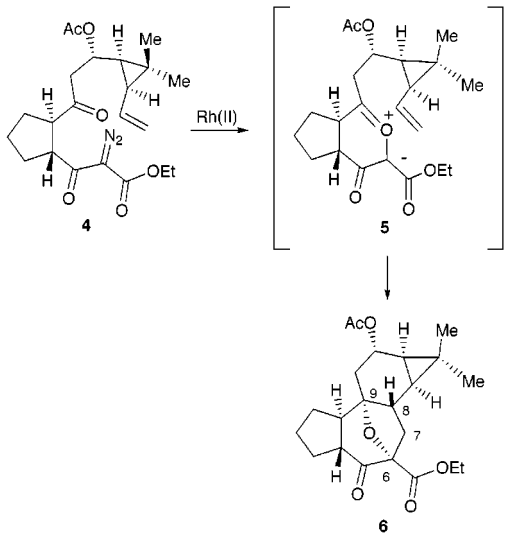
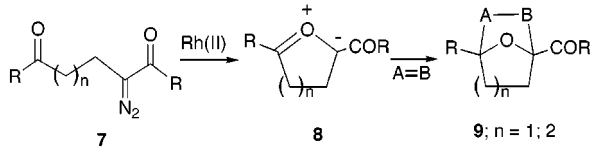
10.1021/jo000378f CCC: $19.00
Published on Web 08/03/2000

Scheme 2



Scheme 3



variety of natural products. An interesting application of this method is found as the central step of Dauben's synthesis of the tigliane ring system.[25] Carbonyl ylide **5**, generated from the diazo carbonyl **4** in the presence of a catalytic amount of rhodium(II) acetate, underwent intramolecular addition with the olefin to form the C_6,C_9-oxido bridged tigliane ring system **6** (Scheme 2). The two new stereocenters at C-8 and C-9 were formed with the correct configurations relative to C-14 and C-15 presented by the natural tigliane compounds.

Of the many unexplored questions concerning the factors that govern the formation of carbonyl ylides by this method, one that is very easy to formulate focuses upon the course of the reaction as a function of the location of the diazo center. Because of the vast array of pathways available to keto carbenoids and the demonstrated susceptibility of these intermediates to both steric and electronic effects, we felt that a systematic study of the related 3-diazoalkanedione system (i.e., **7**) would be of some synthetic interest, as it could be used for the construction of a variety of polyoxy bicyclic rings (Scheme 3). In this paper we detail our observations dealing with the effect of diazo group location on the tandem cyclization−cycloaddition reaction.

Results and Discussion

To investigate the scope of the Rh(II)-catalyzed *cyclization−cycloaddition cascade* of 3-diazoalkanediones and the suitability of this reaction as a general synthetic method, we needed an efficient synthesis of this system. The approach we selected, which allowed for good versatility in assembling different 3-diazoalkanediones, involved a diazo transfer reaction.[26] It is well-known that direct diazo transfer to a ketone enolate is not a particularly efficient reaction.[27] Instead, generation of the diazo group is usually achieved by a "*deacylation diazo transfer*" strategy in which the ketone is first acylated and then treated with a sulfonyl azide reagent such as arylsulfonyl azide in the presence of base.[27,28] Application of this method to the preparation of a variety of diazo carbonyl compounds is well documented in the literature.[29−31] The starting material that we used for the preparation of diazo ketones **11**−**14** corresponded to the tricarbonyl compound **10**, which in turn was prepared by the Ni(II)-catalyzed reaction of various β-diketones with vinyl ketones.[32] Highly-resonance-stabilized carbanionic nucleophiles are known to undergo ready conjugate addition to α,β-unsaturated carbonyl compounds to give 1,1,2-triacyl-substituted ethanes in high yield.[33] It is believed that carbonyl addition is a reversible process and that the more stable product from conjugate addition predominates under conditions of thermodynamic control.[34] We tried various methods to effect the deacylation/diazo transfer reaction, including the often-successful combination of *p*-toluenesulfonyl azide and NaH in a variety of solvents,[35] but with only fair success. The use of methanesulfonyl azide and triethylamine in acetonitrile,[26] however, produced the desired 3-diazoalkanedione in very good yield (Scheme 4).

Our investigations of the cascade reaction of this system began with a study of the Rh(II)-catalyzed behavior of 2-diazo-1,5-diphenyl-1,5-pentanedione (**11**). In this particular case, commercially available 1,5-diphenyl-1,5-pentanedione was treated with NaH in benzene at 0 °C, and this was followed by reaction with ethyl formate.

The resulting formylated ketone was allowed to react at room temperature with 2.0 equiv of methanesulfonyl azide in acetonitrile containing 1 equiv of water and 2.0 equiv of triethylamine. Column chromatography on silica gel furnished **11** as a yellow solid in 90% yield. Treatment of **11** with dimethyl acetylenedicarboxylate (DMAD) in the presence of Rh_2OAc_4 at 25 °C furnished cycloadduct **15** in 90% yield. A similar reaction of diazo ketones **12**−**14** with DMAD in the presence of Rh_2OAc_4 afforded the related cycloadducts **16**−**18** in 76%, 88%, and 78% yields,

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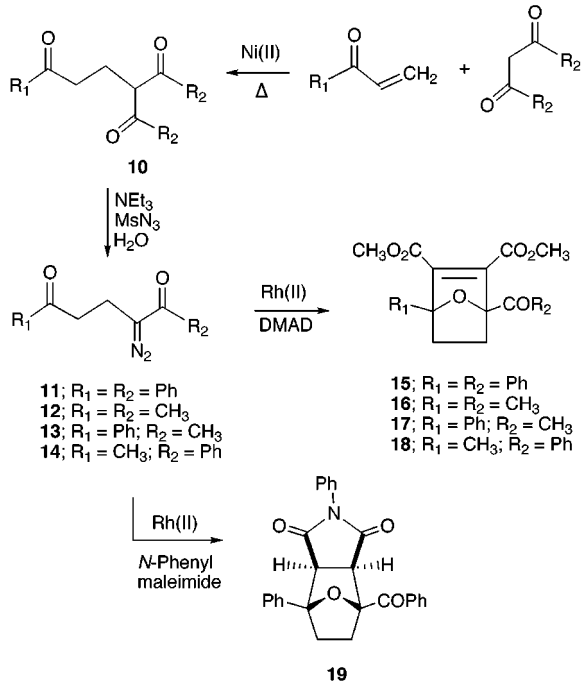
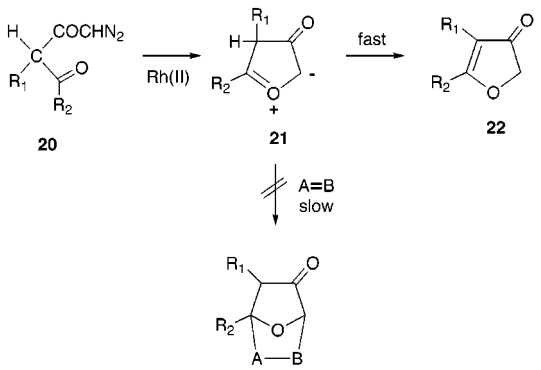
Scheme 4



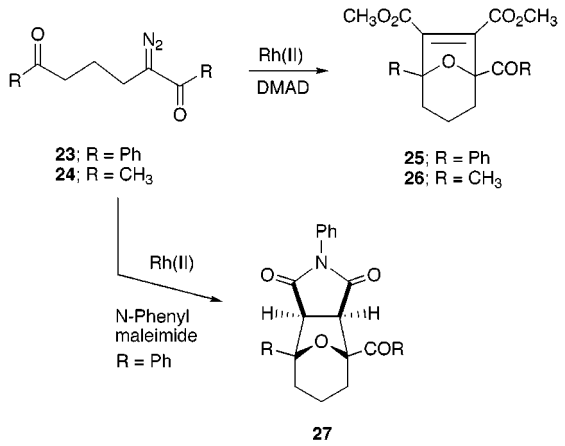
Scheme 5



respectively. It was also possible to trap the five-ring dipole with an electron-deficient olefin. Thus, the reaction of diazo ketone **11** with Rh_2OAc in the presence of *N*-phenylmaleimide gave cycloadduct **19** as a crystalline solid, mp 192−193 °C, in 89% yield. These results are consistent with a mechanism in which the key step involves intramolecular cyclization of the keto carbenoid onto the oxygen atom of the neighboring carbonyl group to give the resonance-stabilized five-membered carbonyl ylide intermediate **8** (Scheme 3), which is trapped by the added dipolarophile. An important point to note is that ylide **8** is sufficiently long lived to undergo bimolecular cycloaddition with DMAD to furnish the cascade adduct (i.e., **15**). In contrast to this result, the closely related five-ring carbonyl ylide **21**, obtained from the reaction of 1-diazobutanedione **20** with Rh_2OAc_4, underwent rapid intramolecular proton transfer to produce furanone **22** (Scheme 5). The expected cycloadduct **23** was not detected in the reaction mixture. More than likely, the difference between the two five-ring ylides is that the α-hydrogen present in ylide **21** is doubly activated and undergoes an internal proton transfer at a very fast rate, thereby preventing the cycloaddition reaction.[37]

Six-ring carbonyl ylides can also participate in these tandem cyclization−cycloaddition reactions. The Rh_2OAc_4-catalyzed reaction of α-diazo ketones **23** and **24** proceeded quite smoothly with DMAD and *N*-phenylmaleimide. With DMAD, cycloadducts **25** and **26** were formed in 90% and 89% yields, respectively. When *N*-phenylmaleimide was used as the trapping agent, cycloadduct **27** was obtained in 90% yield as the exclusive product. The stereochemical assignment of **27** (as well as **19**) was made on the basis of related reactions encountered in our laboratory where the bimolecular cycloaddition was found to occur *endo* with respect to the carbonyl ylide dipole.[40] The above results indicate that intramolecular cyclization to generate six-ring carbonyl ylide dipoles is just as efficient as the formation of five-ring dipoles (Scheme 6).

Scheme 6



In an effort to further extend the cyclization cascade to other carbonyl-containing diazo substrates, we opted to study the Rh(II)-catalyzed behavior of several α-diazo ketoesters and amides. With this goal in mind, we first examined the Rh_2OAc_4-catalyzed reaction of diazo ketoesters **28**−**30**. When the Rh(II)-induced reaction was carried out in the presence of DMAD at room temperature, the cascade cycloadducts **31**−**33** were isolated in 91%, 73%, and 92% yield, respectively (Scheme 7).

Having established that α-diazo ketoesters can undergo the tandem cascade, we decided to explore the intramolecular reaction of a diazo ketoester which contained a suitably positioned C−C double bond. To this end, α-diazo ketoester **34** was prepared and treated with Rh_2OAc_4 at 25 °C to furnish cycloadduct **35** in 80% yield (Scheme 8). When DMAD was added to the reaction mixture, it was possible to isolate the bimolecular adduct **36** in 85% yield. Apparently, the intramolecular cycloaddition of the dipole to the unactivated π-bond is sufficiently slow to allow the carbonyl ylide to react exclusively with the more reactive acetylenic π-bond.

We attempted to carry out a related internal cycloaddition using a system where the tethered alkenyl group resided on the ester portion of the molecule. This led us to study the cycloaddition chemistry of diazo ketoester **37**. When the Rh(II)-catalyzed reaction of **37** was per-

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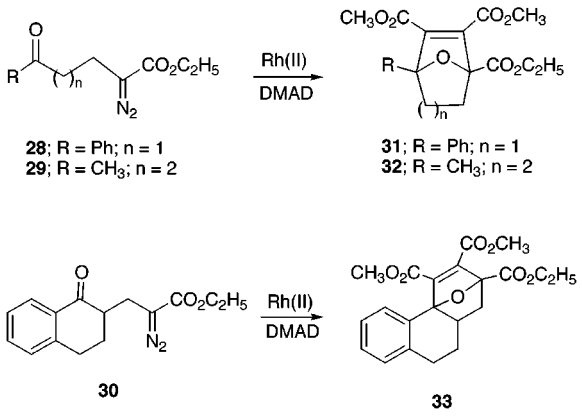
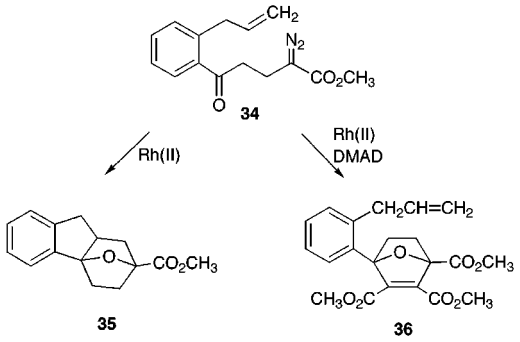
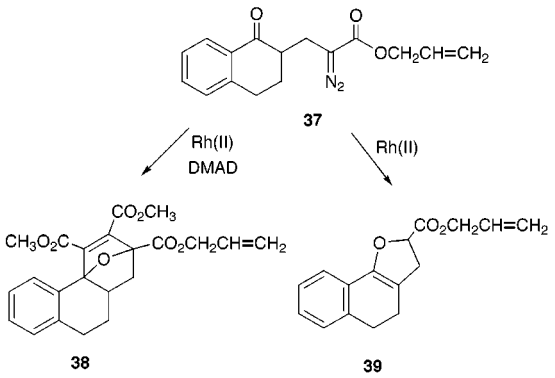
Scheme 7



Scheme 8



Scheme 9



formed in the presence of DMAD, cycloadduct **38** was obtained in 89% yield (Scheme 9). However, in the absence of any trapping agent, no internal cycloadduct could be detected. Instead, the only identifiable compound obtained from this reaction (68%) corresponded to dihydrofuran **39**. The formation of **39** is best rationalized by a hydrogen shift of the initially produced dipole.[38,39] More than likely, the failure to trap the dipole is related to conformational factors. It is well recognized that the *Z*-conformers of esters are significantly more stable than the corresponding *E*-conformers.[41] In the *Z*-orientation, intramolecular dipolar cycloaddition of the resulting carbonyl ylide cannot occur and instead the dipole collapses by means of a proton transfer to give enol ether **39**.

Our earlier studies in this general area have revealed some unexpected results when a nitrogen atom was incorporated at certain positions of the diazo keto skeleton.[42] One of the more interesting examples that we

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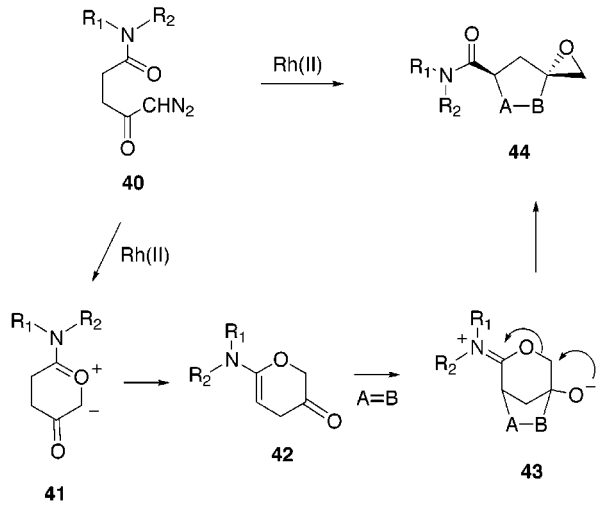
Scheme 10



encountered showed that the amido group can significantly alter the course of the tandem cycloaddition process. Thus, α-diazo carbonyl compounds that possess an amido group in the α-position (i.e., **40**) were found to undergo a rather novel rhodium(II)-catalyzed cycloaddition reaction (Scheme 10).[43] The intramolecular cyclization of the keto carbenoid onto the oxygen atom of the amide generated a push−pull carbonyl ylide dipole (**41**) as a transient species. This highly stabilized dipole did not undergo the 1,3-dipolar cycloaddition readily, but instead underwent proton transfer to produce a cyclic ketene *N*,*O*-acetal (**42**). The nucleophilic π-bond present in **42** added to the activated π-bond of the dipolarophile (A═B) to give a zwitterion intermediate (**43**). This step is followed by epoxide ring formation with charge dissipation, leading to the amido-substituted spirocyclopentyl epoxide **44**.

As a consequence of these earlier investigations, we felt that it would be interesting to extend our studies to include several α-diazo amides to more clearly define the scope and generality of the amido carbenoid cascade. Diazo ketoamide **45** was our first target, and this compound was easily synthesized starting from *N*-(hydroxymethyl)phthalimide and 2,4-pentanedione (see the Experimental Section). We were gratified to find that treating a sample of **45** at 25 °C with DMAD and Rh_2OAc_4 furnished the cascade adduct **46** in 68% yield. Two minor products were also isolated and were assigned as the diazo dipolar cycloadducts **48** (21%) and **49** (7%). When the reaction of **45** was carried out in the absence of Rh_2OAc_4, the same two compounds were obtained, but now in 68% and 22% yields, respectively (Scheme 11). The formation of these substituted pyrazoles can best be explained by a rapid 1,3-dipolar cycloaddition of the starting α-diazo ketone across the activated acetylenic π-bond to give the transient dipolar cycloadduct **47**, which undergoes a subsequent van Alphen−Hüttel rearrangement[44] to furnish the observed products. The major pyrazole is that derived from a preferential 1,5-acetyl shift.[45]

We attempted to apply the intramolecular cyclization−cycloaddition sequence to several closely related diazo

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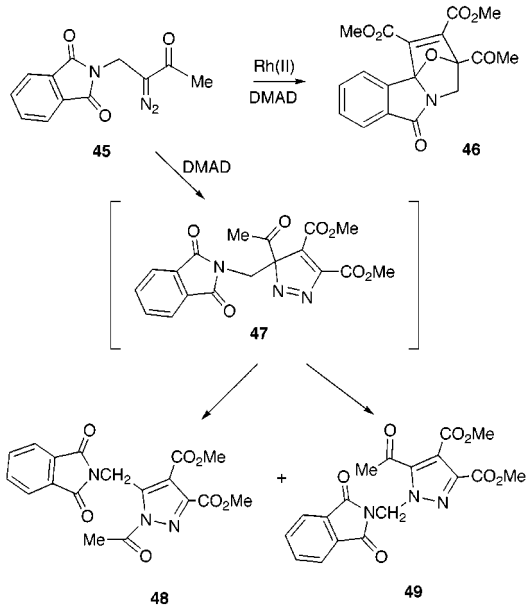
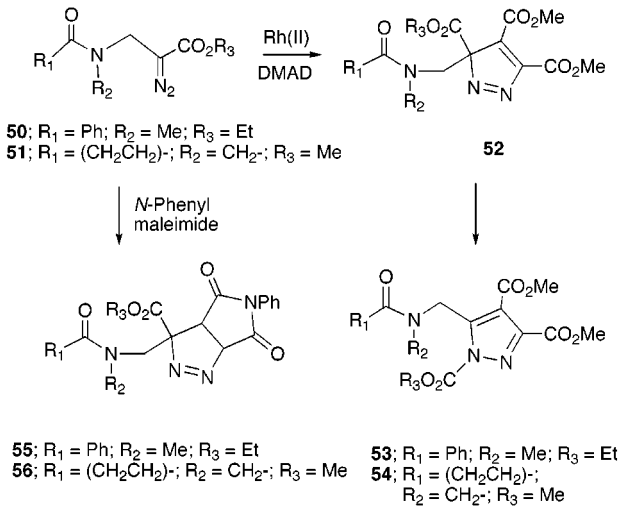
Scheme 11



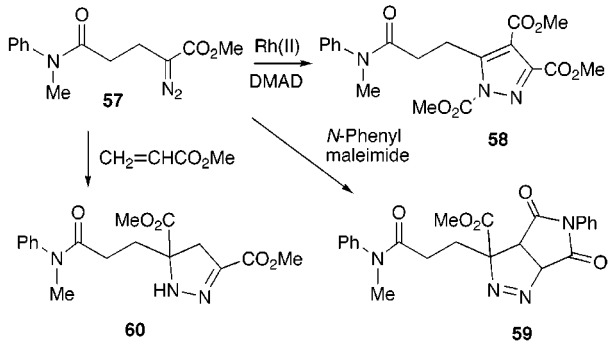
Scheme 12



amidoesters such as **50** and **51** with the hope that these substrates would also undergo a reaction similar to that encountered with diazo ketoamide **45** (i.e., **45** → **46**). Unfortunately, no cascade adduct derived from a carbonyl ylide intermediate could be detected in the crude reaction mixture. The only products obtained when DMAD was used as the trapping dipolarophile corresponded to the rearranged pyrazoles **53** and **54** (Scheme 12). A van Alphen-Hüttel rearrangement of the initially formed dipolar cycloadduct **52** nicely rationalizes their formation. A variety of experimental conditions using different rhodium(II) catalysts in varying quantities were investigated, but in no case were we able to obtain a product derived from the cyclization of a rhodium carbenoid intermediate. It would appear as though the bimolecular 1,3-dipolar cycloaddition of the diazo ester to the activated alkyne proceeds at a much faster rate than the rhodium-catalyzed loss of nitrogen from the starting diazo compound. When *N*-phenylmaleimide was employed as the trapping dipolarophile, dipolar cycloadducts **55** and **56** were isolated as the exclusive products and were obtained in 70% and 83% isolated yielda, respectively.

(45) Schless, P.; Stalder, H. *Tetrahedron Lett.* **1980**, 1417.

Scheme 13



One final point has to do with the rhodium(II)-catalyzed reaction of 2-diazo-4-(methylphenylcarbamoyl)-butyric acid methyl ester (**57**). All of our attempts to obtain a cascade adduct derived from a carbonyl ylide intermediate with this system failed. Several types of dipolarophiles were examined, but only the standard dipolar cycloadducts of the starting diazo compound with the activated π-bonds were isolated (Scheme 13).

In conclusion, the model studies described in this paper demonstrate that the rhodium(II)-catalyzed reaction of 3-diazoalkanediones occurs with high efficiency and represents a useful approach toward the synthesis of various oxabicyclo ring systems. Diazo ketoesters and imides were found to undergo the rhodium(II)-catalyzed cascade cycloaddition in high yield. In contrast, α-diazo amidoesters are reluctant to form the key rhodium carbenoid intermediate, and the major reaction involves 1,3-dipolar cycloaddition of the diazo portion of the molecule with the added dipolarophile. We are continuing to explore the scope, generality, and synthetic applications of the Rh(II) cascade reaction of other diazo carbonyl substrates 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 flame-dried glassware under an atmosphere of dry argon. 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. All solids were recrystallized from ethyl acetate/hexane for analytical data.

2-Diazo-1,5-diphenyl-1,5-pentanedione (11). To a suspension containing 1.0 g (25 mmol) of 60% NaH in 50 mL of benzene at 0 °C was added two drops of anhydrous methanol followed by 2.5 g (10 mmol) of 1,5-diphenyl-1,5-pentanedione in 5 mL of benzene and 1.6 mL (25 mmol) of ethyl formate. The mixture was allowed to warm to rt and was stirred for an additional 12 h, and then 2.4 g (19 mmol) of methanesulfonyl azide and 1.2 mL of triethylamine were added. The mixture was stirred for an additional 4 h, quenched with water, and extracted with ether. The mixture was washed with 10% NaOH and a brine solution, and the organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel to give 1.0 g (90%) of **11** as a yellow solid: mp 52−53 °C; IR (neat) 2082, 1684, 1607, 1347, and 702 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.92 (t, 2H, J = 6.1 Hz), 3.39 (t, 2H, J = 6.1 Hz), and 7.36−7.98 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.6, 36.2, 67.1, 127.0, 127.9, 128.4, 128.5, 131.2, 133.3, 136.3, 137.4, and 199.1. Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.09; N, 10.07. Found: C, 73.32; H, 5.10; N, 9.96.

Dimethyl 1-Phenyl-4-benzoyl-7-oxabicyclo[2.2.1]-2-heptene-2,3-dicarboxylate (15). To a solution containing 0.16 g (0.6 mmol) of diazo ketone **11** in 3 mL of CH_2Cl_2 was added 0.16 g (1.1 mmol) of DMAD in 2 mL of CH_2Cl_2 followed by the addition of 2 mg of rhodium(II) acetate. The mixture was stirred at rt for 30 min, and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography to give 0.23 g (90%) of **15** as a colorless oil: IR (neat) 1725, 1688, 1440, and 1264 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.05 (ddd, 1H, J = 12.1, 8.0, and 4.5 Hz), 2.25−2.40 (m, 2H), 2.68 (ddd, 1H, J = 12.4, 8.0, and 4.2 Hz), 3.64 (s, 3H), 3.65 (s, 3H), and 7.37−8.19 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 30.1, 30.4, 52.2, 52.3, 90.0, 93.5, 126.7, 128.2, 128.3, 128.8, 129.8, 133.4, 135.1, 135.5, 141.8, 146.8, 161.6, 163.5, and 193.2. Anal. Calcd for $C_{23}H_{20}O_6$: C, 70.39; H, 5.14. Found: C, 70.26; H, 5.08.

1-Phenyl-4-benzoyl-2,3-(*N*-phenyl)dicarboxylimide-7-oxabicyclo[2.2.1]heptane (19). To a solution containing 0.3 g (1.1 mmol) of diazo ketone **11** in 8 mL of CH_2Cl_2 was added 0.37 g (2.2 mmol) of *N*-phenylmaleimide followed by the addition of 2 mg of rhodium(II) acetate. The mixture was stirred at rt for 1 h, the solvent was removed under reduced pressure, and the crude residue was chromatographed on a silica gel column to give 0.4 g (89%) of **19** as a white solid: mp 192−193 °C; IR (neat) 1717, 1700, 1385, and 1190 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.07 (ddd, 1H, J = 12.6, 9.2 and 4.0 Hz), 2.25−2.53 (m, 3H), 3.43 (d, 1H, J = 7.1 Hz), 3.88 (d, 1H, J = 7.1 Hz), 7.03 (dd, 2H, J = 7.2 and 1.3 Hz), 7.22−7.53 (m, 10H), 7.57 (d, 1H, J = 7.2 Hz), and 8.23 (d, 2H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.3, 36.6, 43.3, 55.1, 91.6, 92.3, 125.1, 125.9, 128.2, 128.3, 128.8, 129.6, 131.4, 133.3, 135.8, 136.6, 172.9, 173.5, and 196.6. Anal. Calcd for $C_{27}H_{21}NO_4$: C, 76.48; H, 5.00; N, 3.31. Found: C, 76.32; H, 5.07; N, 3.25.

3-Diazo-2,6-heptanedione (12). A mixture containing 1.7 g (10 mmol) of 3-acetyl-2,6-heptanedione,[46] 3.8 g (30 mmol) of methanesulfonyl azide, and 4.3 mL (30 mmol) of triethylamine in 5 mL of CH_3CN was stirred at rt for 1.5 h. The solvent was removed under reduced pressure, and the crude mixture was chromatographed on a silica gel column to give 1.1 g (69%) of **12** as a labile yellow oil which was used in the next step without further purification: IR (neat) 2079, 1709, 1630, 1360, and 1161 cm^{-1}; ^1H NMR ($CDCI_3$, 300 MHz) δ 2.11 (s, 3H), 2.16 (s, 3H), 2.49 (t, 2H, J = 6.0 Hz), and 2.69 (t, 2H, J = 6.0 Hz).

Dimethyl 1-Methyl-4-acetyl-7-oxabicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (16). To a solution containing 0.2 g (1.3 mmol) of α-diazo ketone **12** in 4 mL of heptane and 1 mL of CH_2Cl_2 was added 0.38 g (2.6 mmol) of DMAD followed by the addition of 2 mg of rhodium(II) acetate. The reaction mixture was stirred for 5 h at rt, and the solvent was removed under reduced pressure. The crude residue was purified by silica gel chromatography to give 0.27 g (76%) of **16** as a colorless oil: IR (neat) 1723, 1630, 1431, and 1253 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.70−1.90 (m, 5H), 2.08−2.18 (m, 2H), 2.28 (s, 3H), and 3.78 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.1, 26.2, 30.1, 32.5, 52.0, 52.3, 88.5, 92.6, 143.0, 143.9, 162.7, 162.8, and 203.3. Anal. Calcd for $C_{13}H_{16}O_6$: C, 58.20; H, 6.01. Found: C, 58.29; H, 6.11.

1-Phenyl-4-diazo-1,5-hexanedione (13). A mixture containing 1.3 g (9.6 mmol) of phenyl vinyl ketone, 5 mL (48 mmol) of 2,4-pentanedione, and 0.2 g of $Ni(AcAc)_2$ in 10 mL of dry benzene was heated at 90 °C for 20 h. The solvent was removed under reduced pressure, and the crude residue was chromatographed on silica gel to give 2.1 g (94%) of 1-phenyl-4-acetyl-1,5-hexanedione as a pale yellow oil: IR (neat) 1684, 1597, 1449, and 690 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.16−2.28 (m, 7H), 2.68 (t, 1H, J = 7.8 Hz), 2.97 (t, 1H, J = 6.9 Hz), 3.06 (t, 1H, J = 7.8 Hz), 3.79 (t, 1H, J = 6.9 Hz), and 7.46−7.95 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.7, 29.2, 35.4, 66.6, 127.7, 128.4, 133.0, 136.2, 190.9, and 204.0. Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.38; H, 6.95. Found: C, 72.25; H, 6.94.

(46) Nelson, J. H.; Howells, P. N.; DeLullo, G. C.; Landen, G. L.; Henry, R. A. *J. Org. Chem.* **1980**, *45*, 1246.

To a solution containing 0.7 g (3.0 mmol) of the above triketone in 8 mL of CH_3CN were added 0.6 g (4.5 mmol) of methanesulfonyl azide and 1.2 mL (18.7 mmol) of triethylamine. The resulting solution was stirred for 5 h at rt, the solvent was removed under reduced pressure, and the crude residue was chromatographed on silica gel to give 0.23 g (36%) of **13** as a labile yellow oil which was used in the next step without further purification: IR (neat) 2082, 1684, 1636, and 693 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.19 (s, 3H), 2.72 (t, 2H, J = 6.0 Hz), 3.26 (t, 2H, J = 6.0 Hz), and 7.47−7.95 (m, 5H).

Dimethyl 1-Phenyl-4-acetyl-7-oxabicyclo[2.2.1]-2-heptene-2,3-dicarboxylate (17). To a solution containing 0.12 g (0.6 mmol) of diazo ketone **13** in 2 mL of CH_2Cl_2 was added 0.16 g (1.1 mmol) of DMAD in 2 mL of CH_2Cl_2 followed by the addition of 2 mg of rhodium(II) acetate. After the resulting solution was stirred at 25 °C for 30 min, the solvent was removed under reduced pressure and the crude residue was purified by silica gel chromatography to give 0.16 g (88%) of **17** as a colorless oil: IR (neat) 1734, 1636, 1437, 1258, and 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.87−1.98 (m, 1H), 2.16−2.36 (m, 3H), 2.38 (s, 3H), 3.59 (s, 3H), 3.80 (s, 3H), and 7.34−7.54 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.7, 29.4, 30.7, 52.1, 52.5, 92.3, 92.5, 126.9, 128.2, 128.8, 135.5, 141.6, 146.5, 162.1, 163.1, and 209.9. Anal. Calcd for $C_{18}H_{18}O_6$: C, 65.43; H, 5.50. Found: C, 65.29; H, 5.41.

1-Phenyl-2-diazo-1,5-hexanedione (14). A mixture containing 6.9 g (32 mmol) of 4,4,4-trifluoro-1-phenyl-1,3-butanedione, 5.2 mL (64 mmol) of methyl vinyl ketone, and 0.25 g of $Ni(AcAc)_2$ in 10 mL of benzene was heated at 90 °C for 24 h. The solvent was removed under reduced pressure, and the crude residue was purified on a silica gel column to give 7.7 g (85%) of 1-phenyl-2-trifluoroacetyl-1,5-hexanedione as a labile yellow oil which was used in the next step without further purification: IR (neat) 1715, 1676, 1451, and 693 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.11 (s, 3H), 2.24 (t, 2H, J = 6.6 Hz), 2.60 (t, 2H, J = 6.6 Hz), 5.13 (t, 1H, J = 6.6 Hz), and 7.42−8.10 (m, 5H).

To a solution containing 2.9 g (10 mmol) of the above triketone in 10 mL of CH_3CN were added 1.9 g (15 mmol) of methanesulfonyl azide and 4.2 mL (30 mmol) of triethylamine. The resulting solution was stirred at rt for 3 h, the solvent was removed under reduced pressure, and the crude residue was purified by silica gel chromatography to give 1.5 g (70%) of **14** as a labile yellow oil which was used in the next step without further purification: IR (neat) 2080, 1715, 1609, 1346, and 704 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 2.17 (s, 3H), 2.71 (t, 2H, J = 6.0 Hz), 2.83 (t, 2H, J = 6.0 Hz), and 7.38−7.56 (m, 5H).

Dimethyl 1-Methyl-4-benzoyl-7-oxabicyclo[2.2.1]-2-heptene-2,3-dicarboxylate (18). To a solution containing 0.2 g (0.9 mmol) of diazo ketone **14** in 3 mL of CH_2Cl_2 was added 0.26 g (1.8 mmol) of DMAD in 2 mL of CH_2Cl_2 followed by the addition of 2 mg of rhodium(II) acetate. After the resulting solution was stirred at rt for 30 min, the solvent was removed under reduced pressure and the crude residue was chromatographed on a silica gel column to give 0.24 g (78%) of **18** as a colorless oil: IR (neat) 1723, 1688, 1261, and 889 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.71−1.98 (m, 6H), 2.42−2.53 (m, 1H), 3.62 (s, 3H), 3.81 (s, 3H), and 7.36−8.05 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.4, 30.8, 32.2, 52.2, 52.3, 89.9, 92.4, 128.3, 129.7, 133.4, 134.9, 144.0, 144.1, 162.4, 163.4, and 193.7. Anal. Calcd for $C_{18}H_{18}O_6$: C, 65.43; H, 5.50. Found: C, 65.21; H, 5.37.

2-Diazo-1,6-diphenyl-1,6-hexanedione (23). To a suspension containing 1.0 g (25 mmol) of 60% NaH in 50 mL of benzene at 0 °C was added two drops of anhydrous methanol followed by the addition of 2.7 g (10 mmol) of 1,6-diphenyl-1,6-hexanedione in 5 mL of benzene, and 1.6 mL (25 mmol) of methyl formate. The reaction mixture was allowed to warm to rt and was stirred for 12 h, and then 2.3 g (18 mmol) of methanesulfonyl azide was added. The mixture was stirred for an additional 4 h and was then quenched with water. The solution was extracted with ether and washed with 10% NaOH and a brine solution. The organic layer was dried over

anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The crude residue was purified by silica gel chromatography to give two major products. The minor component contained 1.3 g (57%) of **23** as a yellow solid: mp 73−74 °C; IR (neat) 2072, 1684, 1611, and 1346 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.05 (quint, 2H, J = 7.2 Hz), 2.64 (t, 2H, J = 7.2 Hz), 3.10 (t, 2H, J = 7.2 Hz), 7.37−7.58 (m, 8H), and 7.95 (d, 2H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6, 23.3, 37.1, 66.9, 127.0, 127.9, 128.4, 128.5, 131.3, 133.0, 136.6, 137.5, 189.4, and 199.1. Anal. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.94; H, 5.52; N, 9.59. Found: C, 73.81; H, 5.43; N, 9.46.

Dimethyl 1-Phenyl-5-benzoyl-8-oxabicyclo[3.2.1]-6-octene-6,7-dicarboxylate (25). To a solution containing 0.15 g (0.5 mmol) of diazo ketone **23** in 2 mL of CH_2Cl_2 was added 0.1 g (0.7 mmol) of DMAD in 2 mL of CH_2Cl_2 followed by the addition of 2 mg of rhodium(II) acetate. After the resultant solution was stirred at rt for 30 min, the solvent was removed under reduced pressure and the crude residue was chromatographed on a silica gel column to give 0.19 g (90%) of **25** as a colorless oil: IR (neat) 1727, 1690, 1449, and 1262 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.85−2.09 (m, 5H), 2.33 (dd, 1H, J = 12.2 and 5.2 Hz), 3.69 (s, 3H), 3.73 (s, 3H), 7.31−7.49 (m, 7H), 7.56 (t, 1H, J = 7.0 Hz), and 8.16 (d, 2H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.8, 25.0, 27.6, 52.2, 52.4, 91.0, 92.1, 125.6, 128.1, 128.2, 129.9, 132.9, 135.1, 138.5, 138.9, 142.8, 162.2, 162.5, and 194.9. Anal. Calcd for $C_{24}H_{22}O_6$: C, 70.91; H, 5.46. Found: C, 70.84; H, 5.27.

1-Phenyl-5-benzoyl-6,7-(*N*-phenyl)dicarboxylimide-8-oxabicyclo[3.2.1]octane (27). To a solution of 0.1 g (0.4 mmol) of α-diazo ketone **23** in 4 mL of CH_2Cl_2 was added 0.1 g (0.6 mmol) of *N*-phenylmaleimide followed by the addition of 2 mg of rhodium(II) acetate. The mixture was stirred at rt for 1 h, and the solvent was removed under reduced pressure. The crude residue was purified by silica gel chromatography to give 0.15 g (90%) of **27** as a white solid: mp 178−179 °C; IR (neat) 1717, 1698, 1383, and 1202 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.85−2.08 (m, 4H), 2.33 (dd, 1H, J = 12.9 and 3.0 Hz), 2.44 (d, 1H, J = 11.7 Hz), 3.60 (d, 1H, J = 7.6 Hz), 3.90 (d, 1H, J = 7.6 Hz), 6.79 (dd, 2H, J = 8.0 and 2.2 Hz), 7.20−7.58 (m, 11H), and 8.10 (d, 2H, J = 7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.8, 32.8, 36.0, 52.9, 54.3, 88.1, 90.5, 124.9, 125.8, 127.8, 127.9, 128.1, 128.3, 128.8, 129.7, 131.3, 132.5, 136.3, 139.5, 173.3, 173.6, and 198.8. Anal. Calcd for $C_{28}H_{23}NO_4$: C, 76.87; H, 5.30; N, 3.20. Found: C, 76.69; H, 5.33; N, 3.23.

3-Diazo-2,7-octanedione (24). To a solution containing 3.0 g (30 mmol) of 2,4-pentanedione in 30 mL of THF was slowly added 30 mL of a 1 M THF solution of potassium *tert*-butoxide followed by the addition of 3.2 g (15 mmol) of 5-iodo-2-pentanone. The resulting solution was heated at reflux for 20 h. To this mixture was added a 1 N HCl solution, the mixture was extracted with ether and washed with water, and the organic layer was dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the crude residue was chromatographed on a silica gel column to give 1.5 g (54%) of 3-acetyl-2,7-octanedione as a colorless oil (bp 95 °C (0.2 mmHg)): IR (neat) 1717, 1420, 1360, and 1160 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 1.42−1.52 (m, 2H), 1.75−1.85 (m, 2H), 2.10 (s, 3H), 2.15 (s, 6H), 2.44 (t, 2H, J = 7.2 Hz), and 3.59 (t, 2H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.0, 26.9, 28.1, 29.4, 42.5, 67.9, 203.5, and 207.5; Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.26; H, 8.80.

To a solution containing 1.0 g (5.4 mmol) of this triketone in 10 mL of CH_3CN were added 1.0 g (7.8 mmol) of methanesulfonyl azide and 2.3 mL (16.5 mmol) of triethylamine. The resulting solution was stirred at rt for 3 h, the solvent was removed under reduced pressure, and the crude residue was chromatographed on a silica gel column to give 0.7 g (78%) of **24** as a yellow oil which was used in the next step without further purification: IR (neat) 2074, 1715, 1636, 1420, and 1157 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.68−1.82 (m, 2H), 2.11 (s, 3H), 2.20 (s, 3H), 2.31 (t, 2H, J = 7.2 Hz), and 2.46 (t, 2H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.7, 24.8, 29.4, 41.6, 67.8, 190.5, and 203.6.

Dimethyl 1-Methyl-5-acetyl-8-oxabicyclo[3.2.1]-6-octene-6,7-dicarboxylate (26). To a solution containing 0.1 g (0.6 mmol) of **24** in 2 mL of CH_2Cl_2 was added 0.13 g (0.9 mmol) of DMAD in 2 mL of CH_2Cl_2 followed by the addition of 2 mg of rhodium(II) acetate. After the resultant solution was stirred for 30 min at rt, the solvent was removed under reduced pressure and the crude residue was chromatographed on a silica gel column to give 0.15 g (89%) of **26** as a colorless oil: IR (neat) 1725, 1648, 1438, and 1036 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.50 (s, 3H), 1.54−1.65 (m, 4H), 1.72−1.82 (m, 2H), 2.23 (s, 2H), 3.79 (s, 3H), and 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.6, 22.4, 23.9, 25.1, 29.1, 52.2, 52.4, 87.4, 92.2, 140.3, 140.7, 162.9, 163.1, and 205.0. Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.55; H, 6.43. Found: C, 59.29; H, 6.37.

Ethyl 5-Phenyl-2-diazo-5-oxopentanoate (28). A mixture containing 1.2 g (9.1 mmol) of phenyl vinyl ketone, 5 mL of ethyl acetoacetate, and 0.2 g of $Ni(AcAc)_2$ in 10 mL of dry benzene was heated at 90 °C for 20 h. The solvent was removed under reduced pressure, and the crude residue was purified by silica gel chromatography to give 2.1 g (90%) of ethyl 5-phenyl-2-acetyl-5-oxopentanoate as a colorless oil: IR (neat) 1740, 1717, 1686, 1150, and 691 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 1.26 (t, 3H, J = 7.2 Hz), 2.22−2.32 (m, 5H), 3.05 (t, 2H, J = 7.2 Hz), 3.63 (t, 1H, J = 7.2 Hz), 4.17−4.26 (m, 2H), and 7.44−7.95 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.9, 22.0, 28.9, 35.4, 58.2, 61.3, 127.8, 128.4, 133.0, 136.4, 169.4, 198.7, and 202.8. Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.67; H, 6.92. Found: C, 68.52; H, 6.97.

To a solution containing 0.5 g (2.0 mmol) of the above compound in 5 mL of CH_3CN were added 0.5 g (4 mmol) of methanesulfonyl azide and 0.8 mL (6 mmol) of triethylamine. The resulting solution was stirred for 3 h at rt, the solvent was removed under reduced pressure, and the crude residue was purified by silica gel chromatography to give diazo ketoester **28** (85%) as a yellow oil which was used in the next step without further purification: IR (neat) 2095, 1684, 1371, 1175, and 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.25 (t, 3H, J = 7.2 Hz), 2.72 (t, 2H, J = 6.3 Hz), 3.26 (t, 2H, J = 6.3 Hz), 4.19 (q, 2H, J = 7.2 Hz), and 7.43−7.94 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.4, 18.5, 36.6, 60.5, 127.9, 128.5, 133.2, 136.4, 167.4, and 178.7.

2,3-Dimethyl 4-Ethyl 1-Phenyl-7-oxabicyclo[2.2.1]-2-heptene-2,3,4-tricarboxylate (31). To a solution containing 0.14 g (0.6 mmol) of diazo ketoester **28** in 3 mL of CH_2Cl_2 was added 0.17 g (1.2 mmol) of DMAD in 2 mL of CH_2Cl_2 followed by the addition of 2 mg of rhodium(II) acetate. After the resulting solution was stirred at rt for 30 min, the solvent was removed under reduced pressure and the crude residue was purified by silica gel chromatography to give 0.19 g (91%) of **31** as a clear oil: IR (neat) 1746, 1640, 1437, 1265, and 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.31 (t, 3H, J = 7.2 Hz), 1.99 (dt, 1H, J = 9.9 and 3.3 Hz), 2.21 (dt, 1H, J = 9.9 and 3.3 Hz), 2.35 (dt, 1H, J = 10.2 and 3.3 Hz), 2.47 (dt, 1H, J = 10.2 and 3.3 Hz), 3.56 (s, 3H), 3.77 (s, 3H), 4.23−4.41 (m, 2H), and 7.30−7.50 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.9, 30.5, 30.7, 52.1, 52.3, 61.9, 87.9, 92.5, 126.9, 128.1, 128.7, 135.2, 141.0, 146.4, 162.2, 163.1, and 167.0. Anal. Calcd for $C_{19}H_{20}O_7$: C, 63.35; H, 5.60. Found: C, 63.42; H, 5.73.

Ethyl 2-Diazo-5-acetylpentanoate (29). To a solution containing 2.1 g (9.8 mmol) of ethyl 2,5-diacetylpentanoate[47] in 20 mL of CH_3CN were added 1.8 g (14 mmol) of methanesulfonyl azide and 4 mL (29 mmol) of triethylamine. The resulting solution was stirred for 10 h at rt, the solvent was removed under reduced pressure, and the crude residue was washed with 5% NaOH and extracted with ether. The organic layer was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The crude residue was purified by silica gel chromatography to give 1.8 g (66%) of **29** as a yellow oil which was used in the next step without further purification: IR (neat) 2083, 1686, 1371, and 1159 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 1.26 (t, 3H, J = 7.2 Hz), 1.78 (quint, 2H, J = 7.2 Hz), 2.14 (s, 3H), 2.31 (t, 2H, J = 7.2 Hz), 2.49 (t, 2H, J = 7.2 Hz), and 4.20 (q, 2H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.4, 21.7, 22.6, 29.8, 42.0, 60.6, 167.3, and 207.7.

(47) Jager, H.; Keymer, R. *Arch. Pharm. Ber. Dtsch. Pharm. Ges.* **1960**, *293*, 896.

6,7-Dimethyl 5-Ethyl 1-Methyl-8-oxabicyclo[3.2.1]-6-octene-5,6,7-tricarboxylate (32). To a solution containing 0.1 g (0.5 mmol) of diazo ketoester **29** in 2 mL of CH_2Cl_2 was added 0.15 g (1.0 mmol) of DMAD in 2 mL of CH_2Cl_2 followed by the addition of 2 mg of rhodium(II) acetate. After the resultant solutionw as stirred for 30 min at rt, the solvent was removed under reduced pressure and the crude residue was chromatographed on a silica gel column to give 0.12 g (73%) of **32** as a colorless oil: IR (neat) 1725, 1653, 1380, 1296, and 1038 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.22 (t, 3H, $J = 7.2$ Hz), 1.45 (s, 3H), 1.55−1.85 (m, 6H), 3.75 (s, 6H), and 4.18 (dq, 2H, $J = 7.2$ and 1.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.9, 17.6, 22.4, 25.4, 29.0, 52.2, 52.3, 61.7, 87.3, 88.2, 139.4, 140.6, 162.9, 163.3, and 168.3; HRMS calcd for $C_{15}H_{20}O_7$ 312.1209, found 312.1204.

Ethyl 2-Diazo-3-[2-(α-tetralonyl)]propionate (30). A mixture containing 0.8 g (5.1 mmol) of 2-methylene-α-tetralone,[48] 1.3 g (10 mmol) of ethyl acetoacetate, and 0.1 g of $Ni(AcAc)_2$ in 5 mL of dry benzene was heated at 90 °C for 20 h. The solvent was removed under reduced pressure, and the crude residue was purified by silica gel chromatography to give 1.4 g (88%) of ethyl 2-acetyl-3-[2-(α-tetralonyl)]propionate as a colorless oil which was used in the next step without further purification: IR (neat) 1740, 1715, 1682, and 1360 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 1.27 (t, 3H, $J = 7.2$ Hz), 1.90−2.15 (m, 2H), 2.18−2.28 (m, 1H), 2.33−2.40 (m, 4H), 2.45−2.55 (m, 1H), 2.95−3.05 (m, 2H), 3.88−3.99 (m, 1H), 4.19 (q, 2H, $J = 7.2$ Hz), 7.21−7.30 (m, 2H), and 7.46 (t, 1H, $J = 7.2$ Hz), and 7.90−7.95 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.9, 28.2, 28.6, 28.9, 29.5, 44.9, 56.9, 61.2, 126.5, 127.1, 127.7, 128.6, 132.2, 143.6, 169.4, 199.5 and 202.9.

To a solution containing 0.6 g (2 mmol) of the above compound in 8 mL of CH_3CN were added 0.5 g (4 mmol) of methanesulfonyl azide and 0.8 mL (6 mmol) of triethylamine. The resulting solution was stirred at rt for 6 h, the solvent was removed under reduced pressure, and the crude residue was chromatographed on silica gel to give 0.4 g (72%) of **30** as a yellow oil which was used in the next step without further purification: IR (neat) 2095, 1684, 1601, and 1178 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.25 (t, 3H, $J = 7.2$ Hz), 1.85−2.00 (m, 1H), 2.20−2.30 (m, 1H), 2.55−2.65 (m, 1H), 2.70−2.80 (m, 2H), 2.95−3.15 (m, 2H), 4.19 (q, 2H, $J = 7.2$ Hz), 7.24 (d, 1H, $J = 7.8$ Hz), 7.28 (t, 1H, $J = 7.8$ Hz), 7.45 (t, 1H, $J = 7.8$ Hz), and 7.99 (d, 1H, $J = 7.8$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.3, 24.5, 28.6, 28.9, 47.0, 54.6, 60.5, 126.4, 127.1, 128.6, 132.2, 133.3, 143.8, 167.6, and 199.3.

2-Ethyl 3,4-Dimethyl 2,4a-epoxy-1,9,10,10a-tetrahydrophenanthrene-2,3,4-tricarboxylate (33). To a solution containing 0.24 g (0.9 mmol) of diazo ketoester **30** in 3 mL of CH_2Cl_2 was added 0.25 g (1.8 mmol) of DMAD in 2 mL of CH_2Cl_2 followed by the addition of 2 mg of rhodium(II) acetate. After the resulting solution was stirred at rt for 30 min, the solvent was removed under reduced pressure and the crude residue was chromatographed on a silica gel column to give 0.32 g (92%) of **33** as a colorless oil: IR (neat) 1750, 1638, 1240, and 1130 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.30 (t, 3H, $J = 7.2$ Hz), 1.60−1.75 (m, 1H), 1.98−2.08 (m, 1H), 2.12−2.20 (m, 1H), 2.23−2.35 (m, 2H), 2.80−2.90 (m, 2H), 3.60 (s, 3H), 3.81 (s, 3H), 4.20−4.40 (m, 2H), and 7.10−7.40 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.9, 27.9, 29.5, 37.6, 39.7, 52.1, 52.3, 61.8, 88.1, 90.2, 126.3, 128.4, 128.9, 129.4, 130.1, 139.3, 142.8, 146.4, 162.2. 162.3, and 167.0. Anal. Calcd for $C_{21}H_{22}O_7$: C, 65.28; H, 5.74. Found: C, 65.48; H, 5.87.

Methyl 2-Diazo-5-oxo-5-(2-allylphenyl)pentanoate (34). To a mixture containing 1.8 mL (10 mmol) of tetravinyltin in 30 mL of ether was slowly added 28 mL of 1.4 M methyllithium at 0 °C. After being stirred for 30 min, the resulting solution was cannulated into a solution containing 3.2 g (22 mmol) of *o*-allylbenzaldehyde[49] in 40 mL of ether at 0 °C. After being stirred for 2 h at rt, the mixture was poured into a 1.0 N HCl solution. The aqueous phase was extracted with ether, and the organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude residue was chromatographed on a silica gel column to give 3.4 g (90%) of 1-(2-allylphenyl)-2-propen-1-ol as a colorless oil: IR (neat) 3334, 1638, and 1451 cm^{-1}; ^1H NMR ($CDCI_3$, 300 MHz) δ 1.90 (s, 1H), 3.48 (d, 2H, $J = 6.1$ Hz), 4.95−5.50 (m, 5H), 5.90−6.15 (m, 2H), and 7.10−7.50 (m, 4H); ^{13}C NMR ($CDCI_3$, 75 MHz) δ 36.4, 70.9, 114.6, 115.7, 126.5, 127.5, 129.6, 136.8, 137.2, 139.6, and 140.2. Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.69; H, 8.13.

To a solution containing 2.7 g (15.5 mmol) of the above alcohol in 50 mL of CH_2CI_2 was slowly added 6.5 g (30 mmol) of pyridinium chlorochromate at 0 °C. After the resulting solution was stirred for 2 h, 100 mL of ether was added and the mixture was passed through a short pad of silica gel. The solvent was removed under reduced pressure, and the crude residue was chromatographed on a silica gel column to give 1.2 g (45%) of *o*-allylphenyl vinyl ketone as a colorless liquid: IR (neat) 1661, 1402, and 1231 cm^{-1}; ^1H NMR ($CDCI_3$, 300 MHz) δ 3.51 (d, 2H, $J = 6.3$ Hz), 4.95−5.10 (m, 2H), 5.85−6.20 (m, 3H), 6.75 (dd, 1H, $J = 17.4$ and 10.2 Hz), and 7.20−7.45 (m, 4H); ^{13}C NMR ($CDCI_3$, 75 MHz) δ 37.2, 115.8, 125.6, 128.2, 130.4, 130.6, 131.2, 136.5, 136.8, 137.7, 138.9, and 196.3. Anal. Calcd for $C_{12}H_{12}O$: C, 83.68; H, 7.03. Found: C, 83.51; H, 6.92.

A mixture containing 1.3 g (7.6 mmol) of the above ketone, 5 mL of methyl acetoacetate, and 0.2 g of $Ni(AcAc)_2$ was heated at 90 °C for 20 h. The solvent was removed under reduced pressure, and the crude residue was chromotographed on a silica gel column to give 1.8 g (83%) of methyl 2-acetyl-5-oxo-5-(*o*-allylphenyl)pentanoate as a colorless oil: IR (neat) 1744, 1717, 1688, and 1360 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.20−2.30 (m, 5H), 2.93 (d, 2H, $J = 7.2$ Hz), 3.58−3.65 (m, 3H), 3.73 (s, 3H), 4.90−5.05 (m, 2H), 5.86−6.02 (m, 1H), 7.22−7.30 (m, 2H), 7.40 (t, 1H, $J = 7.5$ Hz), and 7.56 (d, 1H, $J = 7.5$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.1, 28.9, 37.6, 38.4, 52.2, 57.9, 115.5, 126.0, 128.0, 131.0, 131.2, 137.2, 137.8, 139.2, 169.8, 202.6, and 203.0. Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.82; H, 6.99. Found: C, 70.72; H, 7.06.

A mixture containing 0.8 g (2.9 mmol) of the above compound, 0.7 g (5.6 mmol) of methanesulfonyl azide, and 1.1 mL (8 mmol) of triethylamine in 6 mL of CH_3CN was stirred at rt for 2 h. The solvent was removed under reduced pressure, and the crude residue was chromatographed on a silica gel column to give **34** (63%) as a yellow oil which was used in the next step without further purification: IR (neat) 2091, 1696, 1437, 1333, and 1111 cm^{-1}; ^1H NMR ($CDCI_3$, 360 MHz) δ 2.70 (t, 2H, $J = 6.5$ Hz), 3.17 (t, 2H, $J = 6.5$ Hz), 3.62 (d, 2H, $J = 6.5$ Hz), 3.75 (s, 3H), 4.95−5.04 (m, 2H), 5.80−6.00 (m, 1H), 7.25−7.35 (m, 2H), 7.42 (t, 1H, $J = 7.5$ Hz), and 7.76 (d, 1H, $J = 7.5$ Hz); ^{13}C NMR ($CDCI_3$, 75 MHz) δ 18.6, 37.8, 39.5, 51.7, 115.5, 126.1, 128.3, 131.2, 131.5, 137.2, 137.6, 139.5, 167.7, and 202.9.

Methyl 2,4a-Epoxy-3,4,9,9a-tetrahydro-1*H*-fluorene-2-carboxylate (35). To a solution containing 0.24 g (0.9 mmol) of diazo ketoester **34** in 10 mL of CH_2CI_2 was added 2 mg of rhodium(II) acetate. After the resulting solution was stirred for 5 h at rt, the solvent was removed under reduced pressure and the crude residue was chromatographed on a silica gel column to give 0.17 g (80%) of **35** as a white solid: mp 97−98 °C; IR (neat) 1738, 1269, and 1105 cm^{-1}; ^1H NMR ($CDCI_3$, 300 MHz) δ 1.85−1.95 (m, 1H), 2.00−2.08 (m, 1H), 2.10−2.25 (m, 2H), 2.33−2.43 (m, 2H), 2.70−2.80 (m, 2H), 3.05−3.18 (m, 1H), 3.78 (s, 3H), 7.20−7.30 (m, 3H), and 7.44 (d, 1H, $J = 7.2$ Hz); ^{13}C NMR ($CDCI_3$, 75 MHz) δ 30.5, 33.5, 38.2, 43.3, 48.8, 52.1, 86.9, 96.8, 124.3, 125.0, 126.3, 129.7, 136.9, 147.0, and 171.8. Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.70; H, 6.56.

Trimethyl 4-(*o*-Allylphenyl)-7-oxabicyclo[2.2.1]-2-heptene-1,2,3-tricarboxylate (36). To a mixture containing 0.3 g (1.1 mmol) of diazo ketoester **34** in 5 mL of CH_2Cl_2 was added 0.33 g (2.3 mmol) of DMAD followed by the addition of 2 mg of rhodium(II) acetate. After the resulting solution was stirred for 1 h at rt, the solvent was removed under reduced pressure and the crude residue was chromatographed on a silica gel column to give 0.36 g (85%) of **36** as a clear oil: IR (neat) 1752,

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(49) Kampmeier, J. A.; Harris, S. H.; Mergelsberg, I. *J. Org. Chem.* **1984**, *49*, 621.

1640, 1437, and 1263 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.90−2.00 (m, 1H), 2.18−2.28 (m, 1H), 2.36−2.46 (m, 1H), 2.54−2.64 (m, 1H), 3.40−3.68 (m, 5H), 3.80 (s, 3H), 3.86 (s, 3H), 4.98−5.08 (m, 2H), 5.84−5.98 (m, 1H), 7.20−7.35 (m, 3H), and 7.43 (d, 1H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.7, 31.3, 37.6, 52.1, 52.5, 52.7, 88.3, 92.5, 115.6, 125.7, 128.4, 129.1, 130.6, 132.2, 137.9, 139.5, 140.8, 146.6, 162.1, 162.9 and 167.6. Anal. Calcd for $C_{21}H_{22}O_7$: C, 65.27; H, 5.73. Found: C, 65.26; H, 5.63.

Allyl 2-Diazo-3-[2-(α-tetralonyl]propionate (37). A mixture containing 1.8 g (11.5 mmol) of 2-methylene-α-tetralone, 1.4 g (10 mmol) of allyl acetoactate, and 0.2 g of $Ni(AcAc)_2$ in 10 mL of benzene was heated at 90 °C for 40 h. The solvent was removed under reduced pressure, and the crude residue was purified by silica gel chromatography to give 2.5 g (84%) of allyl 2-acetyl-3-[2-(α-tetralonyl)]propionate as a colorless oil: IR (neat) 1717, 1682, 1360, and 1221 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 1.85−2.15 (m, 2H), 2.18−2.28 (m, 1H), 2.30−2.40 (m, 4H), 2.44−2.54 (m, 1H), 2.95−3.05 (m, 2H), 3.90−4.05 (m, 1H), 4.61 (d, 2H, J = 5.7 Hz), 5.20−5.37 (m, 2H), 5.80−5.95 (m, 1H), 7.20−7.45 (m, 3H), and 7.90−8.00 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.1, 28.5, 28.8, 29.5, 44.6, 56.7, 65.6, 118.7, 126.3, 126.9, 127.0, 128.5, 131.3, 133.1, 143.5, 168.9, 199.3, and 202.6. Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 72.07; H, 6.75.

A mixture containing 0.5 g (1.7 mmol) of the above compound, 0.4 g (3.3 mmol) of methanesulfonyl azide, and 0.7 mL (5.0 mmol) of triethylamine in 4 mL of CH_3CN was stirred at rt for 5 h. The solvent was removed under reduced pressure, and the crude residue was purified by silica gel chromatography to give allyl 3-[2-(α-tetralonyl]propionate (90%) as a yellow oil which was used in the next step without further purification: IR (neat) 2093, 1686, 1456, and 1124 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.90−2.05 (m, 1H), 2.22−2.35 (m, 1H), 2.56−2.68 (m, 1H), 2.70−2.90 (m, 2H), 2.95−3.15 (m, 2H), 4.65 (d, 2H, J = 5.7 Hz), 5.20−5.40 (m, 2H), 5.80−6.00 (m, 1H), 7.20−7.38 (m, 2H), 7.46 (d, 1H, J = 7.5 Hz), and 7.99 (d, 1H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.5, 28.7, 28.9, 47.0, 65.0, 117.7, 126.5, 127.1, 128.6, 132.1, 132.2, 133.3, 143.8, 167.2, and 199.2.

2-Allyl 3,4-Dimethyl 2,4a-epoxy-1,9,10,10a-tetrahydrophenanthrene-2,3,4-tricarboxylate (38). To a solution containing 0.21 g (0.8 mmol) of diazo ketoester **37** in 2 mL of CH_2CI_2 was added 0.21 g (1.5 mmol) of DMAD in 2 mL of CH_2CI_2 followed by the addition of 2 mg of rhodium(II) acetate. After the resulting solution was stirred at rt for 2 h, the solvent was removed under reduced pressure and the crude residue was chromatographed on a silica gel column to give 0.27 g (89%) of **38** as a colorless oil: IR (neat) 1746, 1435, 1238, and 1128 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.60−1.72 (m, 1H), 1.98−2.08 (m, 2H), 2.23−2.35 (m, 2H), 2.75−2.90 (m, 2H), 3.58 (s, 3H), 3.78 (s, 3H), 4.65−4.80 (m, 2H), 5.22−5.40 (m, 2H), 5.85−6.00 (m, 1H), 7.10−7.25 (m, 3H), and 7.36 (d, 1H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 27.9, 29.5, 37.6, 39.7, 52.1, 52.4, 66.4, 88.1, 90.3, 119.1, 126.4, 128.5, 129.0, 129.4, 130.2, 131.3, 139.3, 142.6, 146.6, 162.2, 163.4, and 166.8. Anal. Calcd for $C_{22}H_{22}O_7$: C, 66.31; H, 5.57. Found: C, 66.23; H, 5.61.

Allyl 2,3,4,5-Tetrahydronaphtho[1,2-*b*]furan-2-carboxylate (39). To a solution containing 0.23 g (0.8 mmol) of diazo ketoester **37** in 10 mL of CH_2Cl_2 was added 2 mg of rhodium(II) acetate. After the resulting solution was stirred for 3 h at rt, the solvent was removed under reduced pressure and the crude residue was chromatographed on a silica gel column to give 0.16 g (68%) of **39** as a clear oil: IR (neat) 1740, 1194, 1065, and 1032 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 2.39 (t, 2H, J = 7.9 Hz), 2.90−3.00 (m, 3H), 3.10−3.20 (m, 1H), 4.70 (d, 2H, J = 5.8 Hz), 5.16 (dd, 1H, J = 10.8 and 6.8 Hz), 5.26 (dd, 1H, J = 10.1 and 1.1 Hz), 5.36 (dd, 1H, J = 16.9 and 1.1 Hz), 5.88−6.00 (m, 1H), and 7.10−7.35 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.9, 28.4, 37.4, 65.7, 77.9, 107.8, 118.6, 120.4, 126.3, 127.1, 127.3, 127.6, 131.6, 135.8, 150.1 and 171.5. Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.97; H, 6.30. Found: C, 74.72; H, 6.18.

***N*-(2-Diazo-3-oxobutyl)phthalimide (45).** To a solution containing 8.9 g (50 mmol) of *N*-(hydroxymethyl)phthalimide and 10 mL of 2,4-pentanedione was slowly added 30 mL of 98% H_2SO_4 at 0 °C. The resulting mixture was stirred at 50 °C for 6 h and then poured into ice−water. The solid was filtered and rinsed with a small amount of water and ether to give 11.6 g (84%) of *N*-(2-acetyl-3-oxobutyl)phthalimide: mp 129−130 °C; IR ($CHCl_3$) 1771, 1715, 1396, and 1346 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.35 (s, 7H), 4.56 (s, 2H), and 7.68−7.85 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.5, 36.3, 105.8, 123.2, 131.7, 134.1, 168.1, and 193.4. Anal. Calcd for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.93; H, 5.02; N, 5.39.

A mixture containing 0.77 g (3 mmol) of the above phthalimide, 0.6 g (4.5 mmol) of methanesulfonyl azide, and 1.3 mL (9 mmol) of triethylamine was stirred at rt for 3 h. The solvent was removed under reduced pressure, and the crude residue was chromatographed on a silica gel column to give 0.65 g (90%) of **45** as a yellow solid: mp 112−113 °C; IR (neat) 2103, 1713, 1626, and 1315 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.21 (s, 3H), 4.66 (s, 2H), 7.73 (s, 2H), and 7.85 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.0, 32.5, 66.5, 123.4, 131.7, 134.1, 167.6, and 189.0. Anal. Calcd for $C_{12}H_9N_3O_3$: C, 59.26; H, 3.73. Found: C, 59.18; H, 3.69.

Dimethyl 3-Acetyl-3,10b-epoxy-3,4,6,10b-tetrahydropyrido[2,1-*a*]isooxindole-1,2-dicarboxylate (46). To a solution containing 0.18 g (0.7 mmol) of diazo imide **45** in 3 mL of CH_2Cl_2 and 2 mL of pentane was added 0.2 g (1.4 mmol) of DMAD followed by the addition of 2 mg of rhodium(II) acetate. The resulting mixture was stirred at rt for 5 h, and the solvent was removed under reduced pressure. The crude residue was chromatographed on silica gel to give 0.18 g (68%) of **46** as a colorless oil: IR (neat) 1721, 1675, 1231, and 1138 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 2.32 (s, 3H), 3.36 (d, 1H, J = 10.1 Hz), 3.66 (s, 3H), 3.75 (d, 1H, J = 10.1 Hz), 3.87 (s, 3H), and 7.60−7.90 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.3, 45.0, 52.5, 52.9, 96.8, 102.7, 124.5, 125.1, 131.9, 132.6, 135.1, 135.6, 139.5, 146.1, 160.5, 161.6, 169.9, and 199.3. Anal. Calcd for $C_{18}H_{15}NO_7$: C, 60.49; H, 4.23; N, 3.92. Found: C, 60.37; H, 3.98; N, 3.81.

***N*-Acetyl-3,4-dicarbomethoxy-5-phthalimidylpyrazole (48).** In addition to compound **46**, two additional compounds (**48** and **49**) were also isolated from the above silica gel chromatography. These same two compounds were also formed by stirring a 0.2 g (0.8 mmol) sample of diazo ketone **45** and 0.2 g (1.4 mmol) of DMAD in 5 mL of benzene at rt. The solvent was removed under reduced pressure, and the crude residue was subjected to silica gel chromatography. The major fraction contained 0.26 g (67%) of **48** as a white solid, mp 138−139 °C; IR ($CHCl_3$) 1721, 1398, 1315, and 1169 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.71 (s, 3H), 3.56 (s, 3H), 3.84 (s, 3H), 5.36 (s, 2H), and 7.60−7.80 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.4, 33.5, 52.4, 52.7, 118.1, 123.3, 131.5, 134.1, 141.8, 144.2, 161.2, 162.2, 167.0, 167.2, and 171.5. Anal. Calcd for $C_{18}H_{15}N_3O_7$: C, 56.11; H, 3.87; N, 10.90. Found: C, 56.04; H, 3.86; N, 10.75.

The minor product isolated from the chromatographic separation contained 0.09 g (22%) of *N*-phthalimidyl-3-acetyl-4,5-dicarbomethoxypyrazole (**49**) as a white solid: mp 175−176 °C; IR ($CHCl_3$) 1713, 1395, 1377, and 1109 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.41 (s, 3H), 3.83 (s, 3H), 3.93 (s, 3H), 5.11 (s, 2H), and 7.65−7.85 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6, 35.4, 52.3, 53.5, 113.5, 123.4, 132.0, 134.1, 138.8, 150.5, 160.7, 161.4, 167.6, 168.7 and 196.2. Anal. Calcd for $C_{18}H_{15}N_3O_7$: C, 56.11; H, 3.87; N, 10.90. Found: C, 56.10; H, 3.92; N, 10.96.

Ethyl 2-Diazo-3-(*N*-benzoyl-*N*-methylamino)propanoate (50). To a suspension containing 0.2 g of sodium hydride (60% in mineral oil) in 6 mL of benzene at 0 °C was added one drop of anhydrous ethanol, followed by the dropwise addition of 0.5 g of methyl 3-(*N*-benzoyl-*N*-methyl)aminopropanoate[50] and 0.4

(50) Thomas, W. B.; McElvain, S. M. *J. Am. Chem. Soc.* **1932**, *54*, 3295.

g of ethyl formate. The reaction was allowed to warm to 25 °C and was stirred for 12 h followed by the addition of 0.5 g of mesyl azide. The mixture was stirred for 4 h and was quenched with water. The organic layer was separated, washed with a 10% NaOH solution, and dried over Na_2SO_4. Removal of the solvent under reduced pressure and chromatography of the residue gave **50** (85%) as a yellow oil which was used in the next step without further purification: IR (neat) 2100, 1695, 1335, 1175, and 1120 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.29 (t, 3H, $J = 7.0$ Hz), 3.08 (s, 3H), 4.25 (q, 2H, $J = 7.0$ Hz), 4.42 (s, 2H), and 7.42 (s, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.8, 37.4, 37.5, 43.0, 60.4, 126.6, 127.7, 129.3, 134.8, 166.5, and 171.9.

1-Carboethoxy-3,4-dicarbomethoxy-5-(*N*-benzoyl-*N*-methyl)aminomethylpyrazole (53). To 5 mL of a benzene solution containing 0.3 g of DMAD and 2 mg of rhodium(II) acetate at 80 °C was added dropwise a solution containing 0.2 g of diazo amide **50** in 1 mL of benzene over a 30 min period. The mixture was heated at reflux for an additional 30 min and was then concentrated under reduced pressure. Silica gel chromatography of the crude oil afforded **53** as a clear oil in 90% yield: IR (neat) 1735, 1660, 1255, and 1073 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.34 (t, 3H, $J = 7.2$ Hz), 3.05 (s, 3H), 3.93 (s, 3H), 3.94 (s, 3H), 4.34 (q, 2H, $J = 7.2$ Hz), 6.15 (brs, 2H), and 7.36−7.53 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.2, 51.9, 52.2, 52.3, 52.5, 61.8, 114.8, 120.7, 126.7, 127.8, 129.6, 134.2, 139.6, 157.1, 160.1, 162.5 and 171.7. Anal. Calcd for $C_{19}H_{21}N_3O_7$: C, 56.56; H, 5.25; N, 10.42. Found: C, 56.41; H, 5.06; N, 10.25.

3-(*N*-Benzoyl-*N*-methylamino)methyl-3-carboethoxy-4,6-dioxo-5-phenyl-3a,4,6,6a-tetrahydropyrrolo[3,4-*d*]pyrazole (55). Treatment of a 0.1 g sample of diazo amide **50** with *N*-phenylmaleimide according to the procedure outlined above afforded **55** in 70% yield after silica gel chromatography: IR (neat) 1725, 1636, 1499, 1385 and 1198 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.17 (t, 3H, $J = 7.0$ Hz), 2.91 (s, 3H), 3.99 (d, 1H, $J = 14.5$ Hz), 4.05−4.40 (m, 3H), 5.10 (d, 1H, $J = 14.5$ Hz), 6.02 (d, 1H, $J = 8.3$ Hz), and 7.10−7.55 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.1, 40.5, 43.9, 51.3, 52.9, 62.6, 95.4, 102.7, 125.7, 126.2, 128.0, 128.5, 128.6, 129.7, 130.3, 134.3, 166.8, 171.7 and 173.0. Anal. Calcd for $C_{23}H_{22}N_4O_5$: C, 63.57; H, 5.11; N, 12.90. Found: C, 63.32; H, 5.06; N, 12.64.

Methyl 2-Diazo-3-(2′-oxo-1′-pyrrolidinyl)propanoate (51). Following the procedure outlined above, a sample of diazo amide **51** was prepared from 2.0 g of methyl 3-(2′-oxo-1′-pyrrolidinyl)propanoate[51] by the diazo transfer method in 80% yield and was used in the next step without further purification: IR (neat) 2100, 1696, 1308, and 1130 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.05 (tt, 2H, $J = 8.0$ and 7.1 Hz), 2.38 (t, 2H, $J = 8.0$ Hz), 3.47 (t, 2H, $J = 7.1$ Hz), 3.78 (s, 3H), and 4.23 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.8, 30.4, 37.8, 47.0, 51.9, 166.8 and 175.8.

5-(2′-Oxo-1′-pyrrolidinyl)methyl-1,3,4-tricarbomethoxypyrazole (54). A mixture containing 0.3 g of diazo amide **51**, 1.2 equiv of DMAD, and 2 mg of rhodium(II) acetate was allowed to stir at rt for 4 h. The crude reaction mixture was subjected to silica gel chromatography. The major product (87%) obtained was a clear oil and was assigned as structure **54** on the basis of its spectral properties: NMR ($CDCl_3$, 300 MHz) δ 2.03 (tt, 2H, $J = 8.0$ and 7.2 Hz), 2.39 (t, 2H, $J = 8.0$ Hz), 3.45 (t, 2H, $J = 8.0$ Hz), 3.93 (s, 3H), 3.94 (s, 3H), 3.96 (s, 3H) and 6.02 (s, 2H). Anal. Calcd for $C_{14}H_{17}N_3O_7$: C, 49.54; H, 5.05; N, 12.39. Found: C, 49.27; H, 4.83; N, 12.17.

3-Carbomethoxy-4,6-dioxo-3-(2′-oxo-1′-pyrrolidinyl)-methyl-5-phenyl-3a,4,6,6a-tetrahydropyrrolo[3,4-*d*]pyrazole (56). The reaction of a 0.1 g sample of diazo amide **51** with *N*-phenylmaleimide according to the procedure outlined above afforded **56** as a clear oil in 83% yield: NMR ($CDCl_3$, 300 MHz) δ 1.95−2.45 (m, 4H), 3.30−3.45 (m, 2H), 3.74 (s, 3H), 3.80 (d, 1H, $J = 15.0$ Hz), 4.05 (d, 1H, $J = 8.4$ Hz), 4.58 (d, 1H, $J = 15.0$ Hz), 5.91 (d, 1H, $J = 8.4$ Hz), and 7.35−7.58 (m, 5H). Anal. Calcd for $C_{18}H_{18}N_4O_5$: C, 58.36; H, 4.90; N, 15.13. Found: C, 58.14; H, 4.76; N, 15.27.

(51) Gribble, G. W. *J. Org. Chem.* **1970**, *35*, 1944.

2-Diazo-4-(methylphenylcarbamoyl)butyric Acid Methyl Ester (57). A solution containing 3.5 g of glutaric anhydride and 4.0 g of *N*-methylaniline in 50 mL of THF was allowed to stir at 25 °C for 3 h and was then concentrated under reduced pressure to give 4-(methylphenylcarbamoyl)butyric acid in 90% yield: mp 97−98 °C. To a solution of this acid in 100 mL of methanol at −15 °C was slowly added 4.0 g of thionyl chloride. The resulting mixture was allowed to warm to 25 °C and was stirred for 4 h. Concentration of the solution under reduced pressure followed by silica gel chromatography gave 6.0 g (95%) of 4-(methylphenylcarbamoyl)butyric acid methyl ester: NMR ($CDCl_3$, 90 MHz) δ 1.96 (sept, 2H, $J = 6.0$ Hz), 2.16 (t, 2H, $J = 6.0$ Hz), 2.31 (t, 2H, $J = 6.0$ Hz), 3.32 (s, 3H), 3.64 (s, 3H), and 7.18−7.50 (m, 5H). This compound was converted to **57** in 73% yield by the standard diazo transfer method: IR (neat) 2091, 1690, 1437, and 1115 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.30 (t, 2H, $J = 6.3$ Hz), 2.54 (t, 2H, $J = 6.3$ Hz), 3.27 (s, 3H), 3.70 (s, 3H), 7.17 (d, 2H, $J = 7.2$ Hz), 7.37 (t, 1H, $J = 7.2$ Hz) and 7.42 (t, 2H, $J = 7.2$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.7, 32.3, 37.2, 51.6, 127.1, 127.8, 129.8, 143.5, and 171.4. Diazo amidoester **57** was used in the next step without further purification.

5-(3′-(*N*-Methyl-*N*-phenylamino-3′-oxo)propyl-1,4,5-tricarbomethoxypyrazole (58). To 5 mL of a benzene solution containing 0.25 g of DMAD and 2 mg of rhodium(II) acetate at 80 °C was slowly added 0.4 g of diazoamide **57** in 2 mL of benzene. The mixture was heated at reflux for 30 min and was then concentrated under reduced pressure and chromatographed on silica gel to give **58** in 89% yield; mp 119−120 °C; IR (neat) 1773, 1738, 1659, 1224, and 1061 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.44 (t, 2H, $J = 7.4$ Hz), 3.25 (s, 3H), 3.53 (t, 2H, $J = 7.4$ Hz), 3.85 (s, 3H), 3.92 (s, 3H), 3.92 (s, 3H), 4.05 (s, 3H), 7.13 (d, 2H, $J = 7.5$ Hz), and 7.24−7.50 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.0, 32.5, 37.2, 52.1, 52.7, 55.3, 115.3, 127.1, 127.7, 129.6, 143.5, 145.7, 149.4, 151.2, 161.7, 161.9, and 170.5. Anal. Calcd for $C_{19}H_{21}N_3O_7$: C, 56.57; H, 5.25; N, 10.41. Found: C, 56.47; H, 5.23; N, 10.37.

3-Carbomethoxy-4,6-dioxo-3-(3′-(*N*-methyl-*N*-phenyl)-amino-3′-oxo)propyl-5-phenyl-3a,4,6,6a-tetrahydropyrrolo-[3,4-*d*]pyrazole (59). Heating a mixture of diazo amide **57** and *N*-phenylmaleimide in benzene at 80 °C with rhodium(II) acetate afforded pyrazole **59** in 81% yield as a white solid: mp 155−156 °C; IR (neat) 1770, 1720, 1646, 1385, and 1195 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.21−2.42 (m, 3H), 2.42−2.61 (m, 1H), 3.24 (s, 3H), 3.35 (d, 1H, $J = 8.2$ Hz), 3.58 (s, 3H), 6.00 (d, 1H, $J = 8.2$ Hz), and 7.10−7.58 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.7, 31.5, 37.4, 46.2, 53.1, 95.0, 102.6, 126.2, 127.1, 128.0, 129.0, 129.2, 129.9, 130.9, 143.4, 166.5, 167.5, 171.1, and 172.4. Anal. Calcd for $C_{23}H_{22}N_4O_5$: C, 63.58; H, 5.10; N, 12.90. Found: C, 63.55; H, 5.11; N, 12.78.

1,5-Dicarbomethoxy-4,5-dihydro-5-(3′-(*N*-methyl-*N*-phenyl)amino-3′-oxo)propylpyrazole (60). Heating a sample of diazo amide **57** with methyl acrylate in refluxing benzene afforded pyrazole **60** in 65% yield as a white solid: mp 125−126 °C; IR (neat) 1720, 1701, 1655, 1260, and 1121 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.02−2.17 (m, 3H), 2.17−2.34 (m, 1H), 2.68 (d, 1H, $J = 17.8$ Hz), 3.25 (s, 3H), 3.35 (d, 1H, $J = 17.8$ Hz), 3.68 (s, 3H), 3.81 (s, 3H), 6.80 (s, 1H), 7.17 (d, 2H, $J = 7.5$ Hz), 7.37 (t, 1H, $J = 7.5$ Hz), and 7.43 (t, 2H, $J = 7.5$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.9, 32.4, 37.3, 39.2, 52.0, 52.8, 72.4, 127.1, 128.0, 129.8, 141.5, 143.5, 162.2, 171.1 and 173.5. Anal. Calcd for $C_{17}H_{21}N_3O_5$: C, 58.78; H, 6.09; N, 12.10. Found: C, 58.51; H, 6.09; N, 12.15.

Acknowledgment. We gratefully acknowledge the National Science Foundation (Grant CHE-9806331) for generous support of this work.

Supporting Information Available: ^{13}C NMR spectrum for compound **32**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO000378F