Stereo and Electronic Effects in the Rhodium(II)-Mediated Synthesis of Polycyclic Lactones and Lactams from α-Diazo Ester and Amide Precursors

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The rhodium(II) carboxylate catalyzed decomposition of several α-diazo esters and amides has been studied. A series of 5-keto-1-diazo acetates were prepared by acylation of α-hydroxy ketones using the (*p*-toluenesulfonyl)hydrazone of glyoxylic acid chloride. Treatment of these compounds with Rh(II) acetate afforded products derived from carbenoid insertion into solvent. When the hydrogen atom of the diazo carbon was replaced with an electron-withdrawing substituent, smooth cyclization occurred to produce a carbonyl ylide dipole which was subsequently trapped with different dipolarophiles. A series of *N*-alkyl-2-diazo-3-oxobutylamides, when treated with a catalytic quantity of rhodium(II) acetate, gave furo[3,4-*c*]furans in good yield. The reaction proceeds *via* addition of a rhodium-stabilized carbenoid onto the acetylenic π-bond to give a vinyl carbenoid which subsequently cyclizes onto the neighboring carbonyl group to produce the furan ring. *N*-Alkynyl-substituted 2-diazoacetamides were also found to cyclize onto the tethered alkyne unit. The resulting rhodium carbenoid can undergo intramolecular and bimolecular cyclopropanation depending on both electronic and conformational factors. Rotamer population of the starting diazoamide was also found to influence product distribution.

Rhodium(II)-catalyzed reactions of α-diazocarbonyl compounds have assumed strategic importance in C-C bond-forming reactions in organic synthesis.[1-9] Intramolecular reactions such as ylide generation[10-15] and carbon-hydrogen insertion[16-25] are facile processes that can be effectively used to construct unique molecular structures. Over the past few years our research efforts have been concerned with the transition metal catalyzed reaction of α-diazo ketones and the application of the resulting carbenoid moiety to the selective formation of polycyclic systems.[26] Two distinct methodologies have been formulated based upon this strategy: *alkyne-carbenoid metathesis* and *tandem cyclization-cycloaddition*. Both of these sequences have allowed the systematic formation of polycyclic systems from simple monocyclic or acyclic precursors.[27] Moreover, analysis of the orbital interactions occurring during the cycloaddition process often allows prediction of the regio- and stereochemical outcome of these reactions.[28-30] A fitting example of the synthetic utility of the tandem cyclization-cycloaddition protocol

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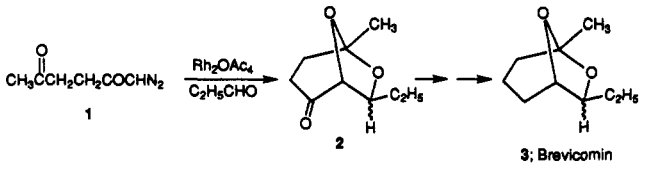
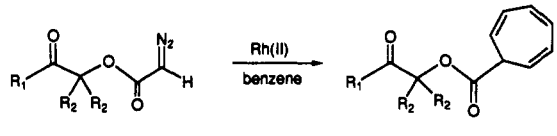
is the recently reported synthesis of both *endo*- and *exo*-brevicomin (**3**), the oxabicyclic ring system being constructed in a single step from an acyclic diazo precursor.[31]



In an effort to further extend these studies to the synthesis of more complex ring systems, we have investigated the possibility of introducing an additional heteroatom into the acyclic skeleton of the diazo precursor. Due to the vast number of nitrogen- and oxygen-based heterocyclic systems, many of which display biological activity, these two heteroatoms appeared to be the logical choice for incorporation. In this paper we wish to detail our observations dealing with the effect of including these heteroatoms into the 1-diazo-2-pentanedione backbone.[32]

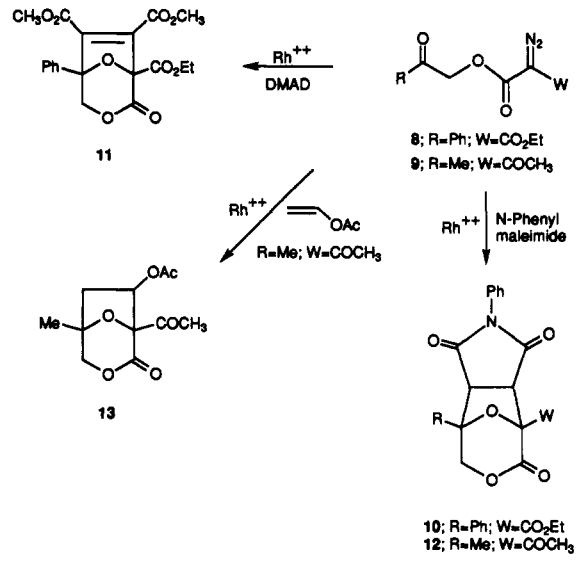
Results and Discussion

Our previous finding that 1-diazo-2,5-pentanedione (**1**) undergoes smooth tandem cyclization–cycloaddition chemistry[28] prompted us to study the closely related diazoacetate system. The 5-keto 1-diazoacetates **4** and **5** were prepared by acylation of the corresponding α-hydroxy ketones with the (*p*-toluenesulfonyl)hydrazone of glyoxylic acid chloride[33] followed by reaction with base. Treatment of **4** with a catalytic amount of rhodium(II) acetate at 25 °C in benzene in the presence of dimethyl acetylenedicarboxylate (DMAD) afforded only cycloheptatriene **6**, the consequence of carbenoid addition to benzene. An analogous reaction occurred with diazoacetate **5**. This result stands in sharp contrast to the corresponding 1-diazo-2,5-alkanedione system (*i.e.*, **1**) which smoothly undergoes the tandem cyclization–cycloaddition reaction under identical reaction conditions.



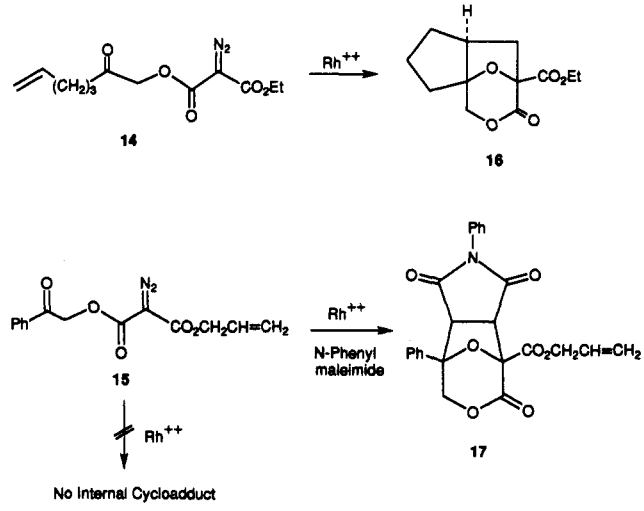
The diminution in electrophilicity of the rhodium carbenoid[34] in the α-diazoacetate system probably attenuates the rate of carbenoid attack on the remote carbonyl group to the point where an alternative reaction pathway can occur. In order to compensate for this diminished electrophilicity, we elected to substitute the hydrogen of the diazo carbon atom with an electron-withdrawing group. Toward this end, the mixed diazomalonate **8** and diazoacetate **9** were synthesized *via* the diazo transfer reaction of the corresponding 1,3-dicarbonyl compound.[35] Reaction

Scheme I



of **8** with rhodium(II) acetate at 80 °C in the presence of *N*-phenylmaleimide (or DMAD) afforded cycloadduct **10** (or **11**) in 65% yield (Scheme I). Cycloaddition of the carbonyl ylide derived from **9** was also carried out in the presence of *N*-phenylmaleimide and vinyl acetate to give cycloadducts **12** and **13**, respectively. The presence of a second carbonyl substituent on the α-diazo carbon increases the electrophilic nature of the carbenoid intermediate, thereby allowing the cyclization reaction to occur. The regio and stereochemistry of the cycloadducts was assigned on the basis of their spectral properties and by FMO considerations.[36]

Having established the validity of increasing the electrophilicity of the intermediate rhodium carbenoid to allow for carbonyl ylide formation, we next explored the intramolecular cycloaddition reaction of a mixed diazomalonate containing a suitably positioned C–C double bond. To this end, diazomalonates **14** and **15** were prepared in a similar manner to compound **8**. Treatment



of **14** with Rh(II) acetate at 80 °C gave the tricyclic lactone **16** in 65% yield. When **15** was treated with rhodium(II) acetate in benzene a complex mixture of products was

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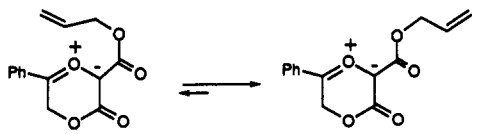
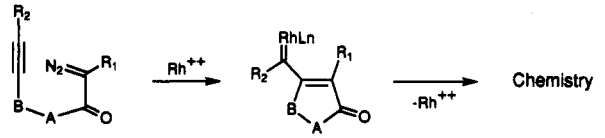
(36) Of the three categories described by Sustmann, type II is particularly common for carbonyl ylides since they possess one of the smallest HOMO–LUMO energy gaps of the common 1,3-dipoles.[30]

obtained that could not be separated, even after extensive chromatography. Examination of the crude NMR spectrum confirmed that the olefinic hydrogens were still present, suggesting that intramolecular dipolar cycloaddition had not taken place. When the decomposition of **15** was repeated in the presence of *N*-phenylmaleimide, carbonyl ylide cycloadduct **17** was isolated in 58% yield. Clearly, the carbonyl ylide was formed but did not undergo intramolecular cycloaddition. The inability of **15** to undergo internal cycloaddition may be related to conformational factors. It is known that the *Z*-conformers of esters are generally more stable than the *E*-conformers.[37] The difference in energy has been measured for methyl formate (4.8 kcal/mol) and for methyl acetate (8.5 kcal/mol).[38] This strikingly large difference in energy would suggest that the equilibrium between the two conformations of the dipole lies predominantly on the side of the *Z*-isomer (*i.e.*, **18b**). In this orientation, intramolecular dipolar cycloaddition cannot occur and instead the dipole collapses to give a myriad of products (*i.e.*, proton loss, attack by nucleophile, dimerization, etc.).[39]



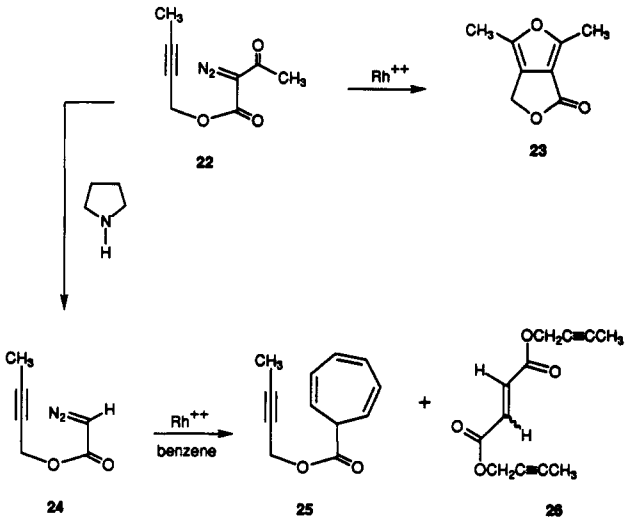
18a **18b**

Having established that dipole formation and subsequent dipolar cycloaddition was possible for distabilized diazo esters, we then turned our attention to the application of these systems to our alkyne-carbenoid metathesis methodology.[40] In an ongoing series of papers,[40] our group, as well as Hoye's,[27] have shown that the rhodium(II)-catalyzed reaction of α-diazo ketones related to **20** results in cyclization of the initially formed metal carbenoid onto the tethered alkyne unit to give an intermediate (**21**), in



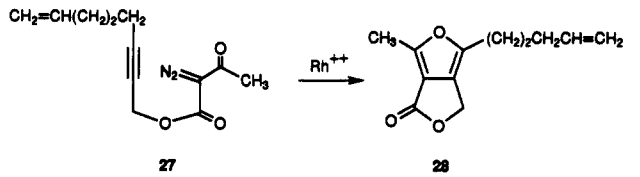
20 **21**

which carbene-like reactivity has been transferred to one of the original alkyne carbon atoms. Much synthetic potential exists by further utilization of the resultant vinyl metallo carbenoid. A series of 2-alkynyl 2-diazo-3-oxobutanoates **20** (R_1 = COR; A = O; B = CH_2), when treated with a catalytic quantity of rhodium(II) acetate, was found to produce furo[3,4-*c*]furans in good yield.[40] Thus, the Rh(II)-catalyzed cyclization of 2-butynyl 2-diazo-3-oxobutanoate (**22**) to furan **23** (75%) was in accord with the earlier observations.[40] However, all attempts to cyclize

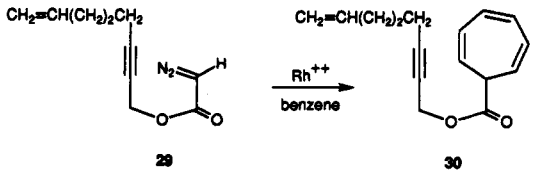


22 **23** **24** **25** **26**

the monostabilized diazo ester **24**, derived from **22** by deacetylization using pyrrolidine, were unsuccessful. No attack on the alkyne tether was observed. Instead, the two major reaction pathways were insertion into the solvent (*i.e.*, benzene) and dimerization, affording cycloheptatriene **25** and fumarate **26**, respectively. The absence of cyclized products derived from **24** again suggests that the initial carbenoid is not electrophilic enough to attack the π-system of the alkyne tether, as previously experienced with diazo esters **4** and **5**. Likewise, the related diazo species **27** afforded furan **28** in good yield, whereas the monostabilized diazo derivative **29** gave only the solvent insertion product **30**. In the former case, the initially cyclized rhodium carbenoid (*i.e.*, **21**; R_1 = $COCH_3$, R_2 = $(CH_2)_3CH{=}CH_2$) prefers to undergo electrocyclization onto the adjacent acetyl group[41] rather than cyclopropanate the nearby alkenyl π-bond.



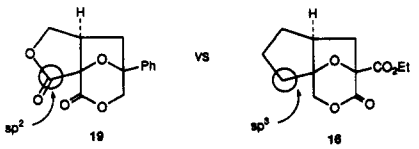
27 **28**



29 **30**

Despite the fact that diazo esters such as **24** and **29** did not appear to undergo attack on the alkynyl π-bond, we

(37) Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 1872.
(38) Blom, C. E.; Gunthard, H. H. *Chem. Phys. Lett.* **1981**, *84*, 267.
(39) The difference in reactivity of diazo esters **14** and **15** may also be related to strain factors. The presence of an additional sp^2 center in the olefinic tether of **15** results in a larger degree of ring strain in the resulting bicyclic product. The larger bond angle of the sp^2 center, as indicated in structure **19**, increases the strain energy of the system to the extent that intramolecular dipolar cycloaddition becomes energetically disfavored. The observed internal cycloadduct **16** possesses an sp^3 center at the corresponding position, creating less strain energy in the system; hence, 1,3-dipolar cycloaddition becomes energetically feasible.

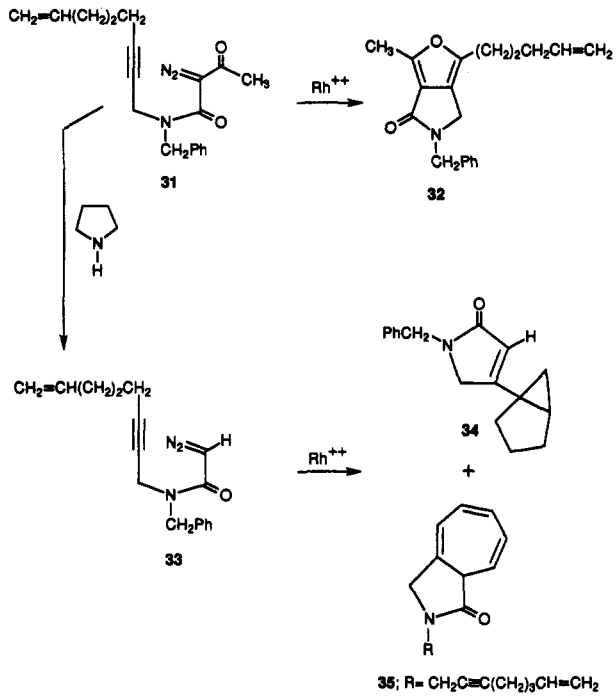


19 **16**

(40) For some leading references see: Padwa, A.; Kinder, F. R. *J. Org. Chem.* **1993**, *58*, 21.

(41) Taylor, E. C.; Turchi, I. J. *Chem. Rev.* **1979**, *79*, 181. Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 947.
(42) Stewart, W. E.; Siddall, T. H. *Chem. Rev.* **1970**, *70*, 517. Rates of rotation of *N,N*-dimethylbenzamides see: Jackman, L. M.; Kavangh, T. E.; Haddon, R. C. *Org. Magn. Reson.* **1969**, *1*, 109. Spaargaren, K.; Korver, P. K.; van der Haak, P. J.; de Boer, Th. *J. Org. Magn. Reson.* **1971**, *3*, 605.

decided to pursue this stragegy and study the corresponding nitrogen analogs. Reaction of the distabilized diazoamide **31** with Rh(II) octanoate gave the bicyclic furan **32** in 83% yield. Once again, electrocyclization of the

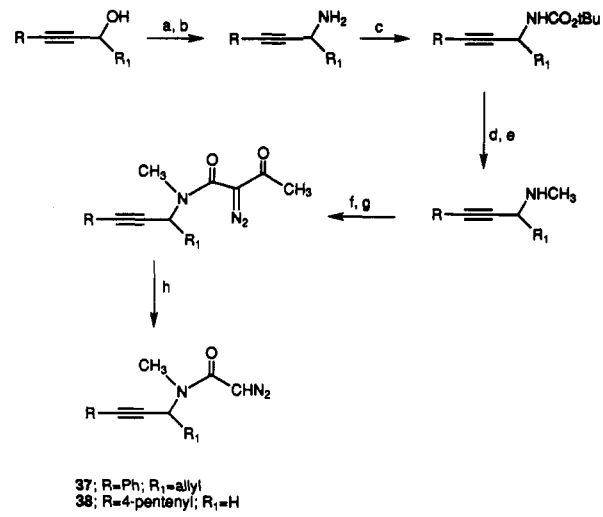


initially formed rhodium carbenoid with the adjacent acetyl group is faster than reaction with the neighboring alkenyl π-system. In order to overcome this problem, we treated **31** with pyrrolidine which produced the simpler diazoamide **33** in 93% yield. In direct contrast to the oxygen case (*i.e.*, **29**), diazoamide **33** was found to undergo attack on the π-system of the acetylenic tether to give a transient vinyl carbenoid which then underwent a further internal cyclopropanation reaction producing **34** in 41% yield. Cycloheptatriene **35** was also isolated from this reaction in 33% and is derived by intramolecular addition of the rhodium carbenoid onto the phenyl ring followed by ring expansion.[6]

The formation of **34** from **33** was of great interest to us. It became apparent that our previous postulate of reduced carbenoid electrophilicity to explain the absence of internal attack products derived from diazo esters **24** and **29** was possibly only one of several contributing factors. Indeed, it is likely that subtle electronic and/or conformational factors dictate the chemical outcome of these reactions. The isolation of both **34** and **35** from **33** suggest that the rotamer population of the starting diazoamide can dictate the outcome of these rhodium(II)-catalyzed reactions. Amide rotamers generally interconvert in solution with lifetimes of 10^{-1}–10^{-2} s.[42,43] The geometry of a typical amide C–N bond will be fixed during the entire lifetime of any acylrhodium carbenoid. Assuming that both amide rotamers are equally reactive toward π-addition, the relative amounts of **34** and **35** that are formed are thus determined by the equilibrium concentrations of the starting rotamers.

The complex nature of the controlling elements in these reactions became even more apparent in our further studies with other related amide systems. In order to remove the competing reaction of aromatic insertion (*i.e.*, **33** → **35**),

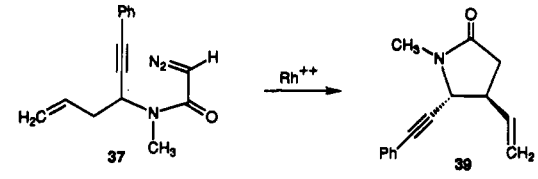
Scheme II



[a] Key: (a) PPh_3, phthalimide, DEAD, THF, rt; (b) KOH, MeOH, NH_2NH_2, H_2O, 65 °C; (c) di-*tert*-butyl dicarbonate, 1,4-dioxane, 90 °C; (d) *n*-BuLi, THF, −78 °C, MeI (e) 5% HCl, THF; (f) diketene, CH_2Cl_2, 0 °C; (g) mesyl azide, Et_3N, benzene, 0 °C; (h) pyrrolidine.

methyl substituted diazo amides **37** and **38** were synthesized by the route shown in Scheme II. The requisite propargyl amines were prepared from the corresponding alcohols via the Gabriel reaction.[43] Monomethylation was accomplished by first protecting the primary amine as its *tert*-butyl carbamate[44] followed by treatment with *n*-butyllithium–MeI and subsequent deprotection with 5% HCl. Reaction of these secondary amines with diketene followed by standard diazo transfer conditions[45] furnished the distabilized diazo species which could be deacetylated using pyrrolidine to produce the desired diazo precursors **37** and **38**.

The Rh(II)-catalyzed decomposition of **37** did not afford the product of internal attack onto the acetylenic π-bond. Instead, only pyrrolidinone **39** was formed in 65% yield



by insertion of the rhodium carbenoid into the allylic C–H bond. The exclusive generation of **39** coincides with the rotamer population of the starting amide. Overlap of the nitrogen nonbonded electrons with the carbonyl π-system fixes the amide conformation so that the larger allylic substituent is oriented toward the rhodium carbenoid center so as to minimize $A^{1,3}$-strain with the methyl group on the nitrogen atom.[46] This places the allylic hydrogens within the reactive environment of the carbenoid center for easy C–H insertion. The sole production of **39** at 25 °C also suggests that at this temperature the rate of C–H insertion is greater than the rate for conformer interconversion.[47,48] When C–H insertion was not a viable option, as in **38**, internal cyclopropanation was again observed

(43) Mitsunobu, O. *Synthesis* **1981**, 1.

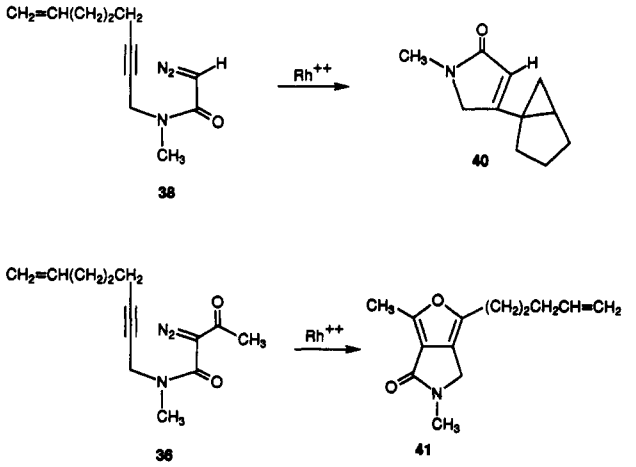
(44) Boger, D. L.; Ishizaki, T.; Kitos, P. A.; Suntornwat, O. *J. Org. Chem.* **1990**, *55*, 5823.

(45) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 733.

(46) Hoffmann, R. W. *Chem. Rev.* **1989**, *89*, 1841.

(47) For a review on conformational changes on reactivity see: Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83.

leading to bicyclohexane 40. As previously shown, decomposition of 36 gave the expected furan 41. The above results clearly demonstrate that conformational effects do indeed play an important role in the outcome of these reactions.



At this point we decided to return to the use of a cyclic system in order to "*lock*" the carbenoid intermediate and acetylenic π-system in close proximity, a tactic that afforded high yields of cyclized products in our previously studied aromatic systems.[26] If we could prepare an appropriate cyclic diazoamide, and if the Rh(II)-catalyzed decomposition of this compound led to a reasonable yield of cyclized product derived from acetylenic π-attack, it would be reasonable to assume that conformational, rather than electronic, factors are the key elements in these reactions. With this in mind, 2-(phenylethynyl)pyrrolidine (43) was synthesized as shown in Scheme III. The *tert*-butylcarbamate of 2-pyrolidinone[48] was treated with 1-(lithiophenyl)acetylene in the presence of boron trifluoride etherate. Reduction of the resulting iminium ion with sodium borohydride[49,50] afforded the free amine upon aqueous workup. Conversion of the amine to the distabilized (42) and monostabilized (43) diazoamides was achieved as previously described. Treatment of the distabilized diazoamide 42 with Rh(II) acetate afforded the expected bicyclic furan 44 in 78% yield. The Rh(II)-catalyzed reaction of ethyl vinyl ether afforded cyclopropyl ether 45 in 84% yield. The formation of 45 can readily be attributed to a tandem cyclization–bimolecular cyclopropanation reaction. The high yielding nature of this reaction clearly indicates that internal alkyne attack is electronically viable, and it is probable that conformational factors dictate the reaction outcome in the acyclic diazoamide systems.

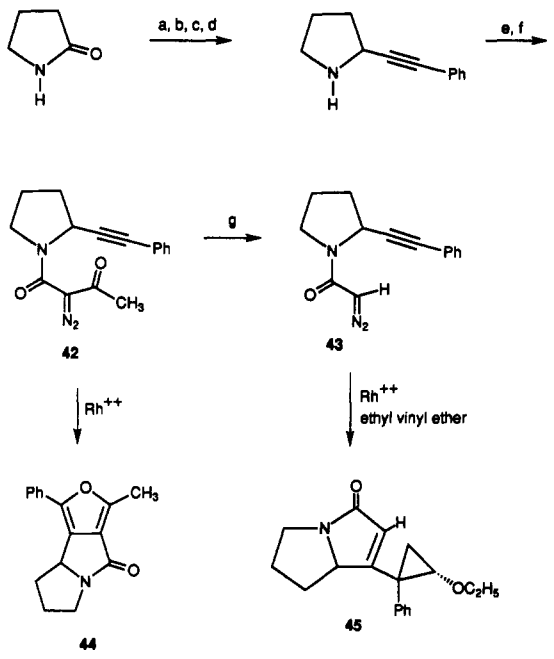
In conclusions, our studies have demonstrated that both carbonyl ylide and alkyne metathesis methodologies can be applied to acyclic diazo esters and amides resulting in the formation of a variety of heteropolycyclic systems. The chemical outcome of these reactions appears to be dependent upon both conformational and electronic factors. Further studies on the mechanism and synthetic potential of these methods are in progress.

(48) Another possibility is that there is a significant diminution in the rate of alkyne attack by the rhodium carbenoid when the acetylenic group contains a phenyl rather than an alkyl substituent, and consequently the rate of insertion into the allylic site is much faster.

(49) Flynn, D. L.; Zelle, R. E.; Grieco, P. A. *J. Org. Chem.* **1983**, *48*, 2424.

(50) Yamaguchi, M.; Hirao, I. *Tetrahedron Lett.* **1983**, *23*, 1719.

Scheme III



[a] Key: (a) di-*tert*-butyl dicarbonate, DMAP, CH_2Cl_2, rt; (b) 1-lithio-2-phenylacetylene, THF, BF_3-OEt_2, −78 °C; (c) MeOH, $NaBH_4$; (d) 10% HCl; (e) diketene, CH_2Cl_2, 0 °C; (f) mesyl azide, Et_3N, benzene, 0 °C; (g) pyrrolidine, rt.

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.

Preparation and Rhodium(II)-Catalyzed Reaction of 2-Oxo-2-phenylpropyl Diazoacetate (4). A flask containing 1.01 g (3.89 mmol) of glyoxyloyl chloride tosylhydrazone and 0.52 g (3.79 mmol) of 2-hydroxyacetophenone in 15 mL of CH_2Cl_2 was cooled to 0 °C, and 1.1 mL (8.0 mmol) of Et_3N in 5 mL of CH_2Cl_2 was added dropwise over 30 min. The resulting yellow solution was stirred at 0 °C for 1 h and then at rt for a further 30 min. Removal of the solvent under reduced pressure followed by chromatography on Florisil gave 0.46 g (62%) of α-diazo ketone 4: IR (neat) 2105, 1710, and 1695 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.95 (bs, 1H), 5.42 (s, 2H), 7.55 (m, 3H), 7.87 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 44.7, 66.1, 127.7, 128.8, 133.9, 134.1, and 192.9.

A solution containing 100 mg (0.9 mmol) of 4 and 104 mg (0.73 mmol) of DMAD in 3 mL of benzene under N_2 was treated with a catalytic amount of rhodium(II) acetate. The resulting solution was immersed in a preheated oil bath, heated at reflux for 1 h, and then concentrated under reduced pressure. The crude solid obtained was chromatographed on silica gel to give 70 mg (56%) of cycloheptatriene 6 which showed the following spectral properties: mp 102–103 °C; IR (neat) 3026, 1740, and 1697 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.77 (m, 1H), 5.48 (s, 2H), 5.61 (dd, 1H, J = 8.9 and 5.5 Hz), 6.32 (bd, 2H, J = 2.9 Hz), and 6.70 (bt, 2H, J = 2.9 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 43.8, 66.4, 116.8, 125.7, 127.8, 128.9, 131.0, 134.0, 134.1, 172.6, and 191.9. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.58; H, 5.55. Found: 75.36; H, 5.42.

Preparation and Rhodium(II)-Catalyzed Reaction of 1,1-Dimethyl-2-oxopropyl Diazoacetate (5). A solution of 1.01 g (3.89 mmol) of glyoxyloyl chloride tosylhydrazone and 0.39 g (3.79 mmol) of 2-hydroxyacetophenone in 15 mL of CH_2Cl_2 was cooled to 0 °C and treated with 1.1 mL (8.0 mmol) in Et_3N in 5 mL of CH_2Cl_2 dropwise over 30 min. The resulting yellow solution was stirred at 0 °C for 1 h and then at rt for a further 30 min. The solution was concentrated under reduced pressure,

and the resulting crude product was chromatographed on Florisil to give 0.13 g (21%) of diazoacetate **5**; IR (neat) 2114, 1735, and 1706 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 6H), 2.12 (s, 3H), and 4.76 (bs, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 23.8, 30.0, 47.6, 169.0, and 201.2.

A solution containing 50 mg (0.29 mmol) of **5** and 62 mg (0.43 mmol) of DMAD in 2 mL of benzene under N_2 was treated with a catalytic amount of rhodium(II) acetate. The resulting solution was heated at reflux for 1 h. Concentration under reduced pressure and subsequent column chromatography on silica gel gave 29 mg (45%) of cycloheptatriene **7** which showed the following spectral properties; IR (neat) 2925, 1742, and 1736 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 1.50 (s, 6H), 2.12 (s, 3H), 2.58 (m, 1H), 5.38 (dd, 2H, J = 8.9 and 5.4 Hz), 6.27 (m, 2H), and 6.65 (bt, 2H, J = 2.8 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 23.4, 29.7, 43.9, 61.3, 116.2, 125.9, 130.9, 172.5, and 201.2; HRMS calcd for $C_{13}H_{16}O_3$ 220.1099, found 220.1098.

Rhodium(II)-Catalyzed Reaction of Ethyl 2-Oxo-2-phenylethyl Diazomalonate (8). A solution containing 1.0 g (7.3 mmol) of 2-hydroxyacetophenone and 1.16 g (8.8 mmol) of ethyl hydrogen malonate in 10 mL of CH_2Cl_2 was treated with 1.67 g (8.1 mmol) of dicyclohexylcarbodiimide and 0.10 g (0.8 mmol) of 4-(dimethylamino)pyridine at 0 °C. The mixture was allowed to warm to rt and was stirred for an additional 5 h. The solution was filtered in order to remove dicyclohexyl urea, and the filtrate was concentrated under reduced pressure. The resulting residue was subjected to flash silica gel chromatography to give 1.2 g (66%) to ethyl 2-oxo-2-phenylethyl malonate as a colorless oil: IR (neat) 1765, 1745, 1710, 1470, and 1380 cm^{-1}; ^1H-NMR ($CDCl_3$, 90 MHz) δ 1.20 (t, 3H, J = 7.0 Hz), 3.55 (s, 2H), 4.25 (q, 2H, J = 7.0 Hz), 5.40 (s, 2H), and 7.85 (m, 5H).

To a solution containing 0.5 g (2.0 mmol) of the above compound and 0.47 g (2.0 mmol) of *p*-acetamidobenzenesulfonyl azide[51] in 5 mL of acetonitrile was added 0.55 mL (4.0 mmol) of Et_3N at 0 °C. The solution was stirred at 0 °C for 1 h and at 25 °C for 2 h. The solvent was removed under reduced pressure, and the resulting residue was taken up in 5 mL of CH_2Cl_2. After filtration, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel chromatography to give 0.25 g (46%) of ethyl 2-oxo-2-phenylethyl diazomalonate (**8**) as a pale yellow oil: IR (neat) 2150, 1770, 1760, 1710, 1380, 1340, and 1110 cm^{-1}; ^1H-NMR ($CDCl_3$, 90 MHz) δ 1.30 (t, 3H, J = 7.0 Hz), 4.35 (q, 2H, J = 7.0 Hz), 5.50 (s, 2H), and 7.90 (m, 5 H).

A solution containing 117 mg (0.42 mmol) of **8** and 220 mg (1.3 mmol) of *N*-phenyl maleimide in 5 mL of benzene was treated with a catalytic amount of rhodium(II) acetate. The solution was placed in a preheated oil bath at 90 °C, and the mixture was heated until N_2 evolution ceased (*ca.* 30 min). After the mixture was cooled to rt, the solid that formed was filtered, the crude product was dissolved in 5 mL of CH_2Cl_2, and the solution was filtered through a pad of Celite. Recrystallization of the residue from hexane gave 120 mg (65%) of the expected dipolar cycloadduct **10** as colorless crystals: mp 209–210 °C; IR (KBr) 1780, 1725, 1505, 1385, and 1190 cm^{-1}; ^1H-NMR ($CDCl_3$ 300 MHz) δ 1.45 (t, 3H, J = 7.2 Hz), 3.93 (d, 1H, J = 7.3 Hz), 4.20 (d, 1H, J = 7.3 Hz), 4.50 (q, 2H, J = 7.2 Hz), 4.67 (d, 1H, J = 11.3 Hz), 4.86 (d, 1H, J = 11.3 Hz), and 7.40 (m, 10 H). Anal. Calcd for $C_{23}H_{19}NO_7$: C, 65.54; H, 4.55; N, 3.33. Found: C, 65.29; H, 4.42; N, 3.19.

A solution containing 50 mg (0.18 mmol) of **8** and 27 mg (0.19 mmol) of DMAD was treated with a catalytic amount of rhodium(II) acetate. The solution was placed in a preheated oil bath at 90 °C and heated until N_2 evolution had ceased (*ca.* 30 min). After being cooled to rt, the solution was filtered through a pad of Celite and the solvent was removed under reduced pressure. The resulting residue was recrystallized from a CH_2Cl_2–hexane mixture to give 45 mg (66%) of the expected dipolar cycloadduct **11** as a white solid: mp 102–103 °C; IR (KBr) 1765, 1745, 1730, 1460, 1440, 1310, and 1260 cm^{-1}; ^1H-NMR (benzene-d_6, 300 MHz) δ 0.92 (t, 3H, J = 7.1 Hz), 3.20 (s, 3H), 3.56 (s, 3H), 4.05 (q, 2H, J = 7.1 Hz), 4.40 (d, 1H, J = 11.3 Hz), 4.62 (d, 1H, J = 11.3 Hz), and 7.01 (m, 5H). Anal. Calcd for $C_{19}H_{18}O_9$: C, 58.45; H, 4.65. Found: C, 58.37; H, 4.38.

(51) Baum, J. S.; Shook, D. A.; Davies, H. M. L.; Smith, H. D. *Synth. Commun.* **1987**, *17*, 1709.

Preparation and Rhodium(II) Acetate Catalyzed Reaction of 2-Oxopropyl 2-Diazo-3-oxobutanoate (9). Using the general procedure of Gilbert and Kelly,[52] a mixture containing 13.0 g (100 mmol) of ethyl acetoacetate, 7.2 g (100 mmol) of 2-methylpropen-1-ol, and 12.2 g (100 mmol) of 4-(*N*,*N*-dimethylamino)pyridine was taken up in 500 mL of anhydrous toluene. To this solution was added 50 g of oven-dried molecular sieves (4 Å), and the mixture was heated at reflux for 24 h. After being cooled to rt, the solution was washed with a saturated NH_4Cl solution and dried over $MgSO_4$. Removal of the solvent under reduced pressure left a crude oil which was chromatographed on silica to give 9.4 g (60%) of a yellow oil whose structure was assigned as 2-methyl-2-propenyl 3-oxobutanoate: IR (neat) 1740, 1715, 1650, 1410, 1360, 1155, and 910 cm^{-1}; ^1H-NMR ($CDCl_3$, 90 MHz) δ 1.76 (s, 3H), 2.26 (s, 3H), 3.53 (s, 2H), 4.60 (s, 2H), and 5.00 (m, 2H).

A stream of ozone was bubbled into a −78 °C solution containing 5.0 g (32.0 mmol) of the above compound in 150 mL of CH_2Cl_2 until the solution turned blue. To this mixture was added 4.0 g (64.4 mmol) of dimethyl sulfide at −78 °C, and the reaction was allowed to warm to rt and stirred overnight. The solvent and excess dimethyl sulfide were removed under reduced pressure, and the resulting crude oil was chromatographed on silica gel to give 4.1 g (81%) of 2-oxopropyl 3-oxobutanoate: IR (neat) 1760, 1740, 1715, 1425, 1365, 1160, and 800 cm^{-1}; ^1H-NMR ($CDCl_3$ 90 MHz) δ 2.16 (s, 3H), 2.30 (s, 3H), 3.53 (s, 2H), and 5.72 (s, 2H).

A 1.33-g (11.0 mmol) sample of methanesulfonyl azide[53] and 1.58 g (10.0 mmol) of the above keto ester were taken up in 20 mL of acetonitrile. To this mixture was added 2.81 mL (38.2 mmol) of dry Et_3N over a 10-min interval. After stirring for 3 h, the solvent was removed under reduced pressure and the crude oil was chromatographed on silica gel to give 0.92 g (50%) of a light yellow solid whose structure was assigned as 2-oxopropyl 2-diazo-3-oxobutanoate (**9**): mp 59–60 °C; IR (neat) 2150, 1740, 1720, 1660, 1330, 1150, and 1095 cm^{-1}; ^1H-NMR ($CDCl_3$, 90 MHz) δ 2.16 (s, 3H), 2.46 (s, 3H), and 4.80 (s, 2H). Anal. Calcd for $C_7H_8N_2O_4$: C, 45.64; H, 4.38; N, 15.22. Found: C, 45.58; H, 4.27; N, 15.09.

A solution containing 200 mg (1.1 mmol) of **9** and 560 mg (3.3 mmol) of *N*-phenylmaleimide in 25 mL of benzene was treated with rhodium(II) acetate. The solution was placed in a preheated 90 °C oil bath and was heated until N_2 evolution had ceased (*ca.* 20 min). Removal of the solvent followed by silica gel chromatography of the residue gave 340 mg (94%) of 8-acetyl-4,6-epoxy-4-methyl-2,3,3a,4,5,7,8,8a-octahydro-1,3,7-trioxo-*N*-phenyl-1*H*-oxepino[4,5-*c*]pyrrole (**12**): mp 245–246 °C; IR (neat) 1765, 1730, 1390, 1215, and 1080 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.47 (s, 3H), 2.50 (s, 3H), 3.95 (d, 1H, J = 7.5 Hz), 4.47 (d, 1H, J = 11 Hz), 4.48 (d, 1H, J = 7.5 Hz), 4.61 (d, 1H, J = 11 Hz), and 7.20–7.55 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 17.7, 50.4, 54.3, 78.1, 79.9, 88.3, 126.6, 128.6, 128.8, 131.9, 162.6, 172.4, 172.8, and 195.4. Anal. Calcd for $C_{17}H_{15}NO_6$: C, 61.99; H, 4.59; N, 4.26. Found: C, 61.87; H, 4.40; N, 4.03.

A solution containing 55 mg (0.30 mmol) of **9** and 86 mg (1.0 mmol) of vinyl acetate in 5 mL of benzene was treated with a 2-mg sample of rhodium(II) acetate. The solution was placed in a 90 °C preheated oil bath and was heated until N_2 evolution had ceased (*ca.* 20 min). After cooling, the solution was filtered and the solvent was removed under reduced pressure. The crude oil was chromatographed on a silica gel column to give 51 mg (75%) of a clear oil whose structure was assigned as 7-acetoxy-1-acetyl-5-methyl-1-oxo-3,8-dioxabicyclo[3.2.1]octane (**13**): IR (neat) 1760, 1740, 1240, 1140, 1075, and 800 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.43 (s, 3H), 2.00 (dd, 1H, J = 14.0 and 4.0 Hz), 2.08 (s, 3H), 2.32 (s, 3H), 2.58 (dd, 1H, J = 14 and 10 Hz), 4.23 (d, 1H, J = 11 Hz), 4.45 (d, 1H, J = 11 Hz), and 5.42 (dd, 1H, J = 10 and 4 Hz). Anal. Calcd for $C_{11}H_{14}O_6$: C, 54.53; H, 5.83. Found: C, 54.38; H, 5.72.

Preparation and Rhodium(II) Acetate Reaction of Ethyl 2-Oxo-6-heptenyl Diazomalonate (14). A solution containing 4.0 g (20.9 mmol) of 1-bromo-6-hepten-2-one[54] and 8.95 g (131

(52) Gilbert, J. C.; Kelly, T. A. *J. Org. Chem.* **1988**, *53*, 449.
(53) Taber, D. F.; Ruckle, R. E., Jr.; Hennessy, M. J. *J. Org. Chem.* **1986**, *51*, 4077.
(54) Oppolzer, W.; Battig, K.; Hudlicky, T. *Tetrahedron* **1981**, *37*, 4359.

mmol) of sodium formate in 60 mL of 95% ethanol was heated at reflux for 15 h. The solvent was removed under reduced pressure, and the resulting residue was taken up in 50 mL of water. The aqueous solution was extracted with CH_2Cl_2, and the combined organic extracts were washed with 50 mL of brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the resulting residue was subjected to flash silica gel chromatography to give 2.05 g (75%) of 1-hydroxy-6-hepten-2-one as a light yellow oil: IR (neat) 1940, 1735, 1440, 1420, and 1070 cm^{-1}; ^1H-NMR ($CDCl_3$, 90 MHz) δ 1.80 (m, 2H), 2.05 (t, 2H, J = 7.5 Hz), 2.42 (t, 2H, J = 7.5 Hz), 3.25 (t, 1H, J = 4.5 Hz), 4.30 (d, 2H, J = 4.5 Hz), 5.10 (m, 2H), and 5.75 (m, 1H).

A solution containing 0.75 g (6.0 mmol) of the above alcohol and 0.82 g (6.2) of ethyl hydrogen malonate in 10 mL of CH_2Cl_2 was treated with 1.33 g (6.45 mmol) of dicyclohexyl carbodiimide and 70 mg (0.6 mmol) of 4-(dimethylamino)pyridine at 0 °C. The solution was allowed to warm to rt and was further stirred for an additional 15 h. The solution was filtered so as to remove dicyclohexyl urea, and the filtrate was concentrated under reduced pressure. The resulting residue was subjected to flash silica gel chromatography to give 1.04 g (74%) of ethyl 2-oxo-6-heptenyl malonate as a clear oil: IR (neat) 1765, 1745, 1420, and 1150 cm^{-1}; ^1H-NMR ($CDCl_3$, 90 MHz) δ 1.32 (t, 3H, J = 7.0 Hz), 1.75 (m, 2H), 2.05 (m, 2H), 2.46 (t, 2H, J = 6.5 Hz), 3.55 (s, 2H), 4.30 (q, 2H, J = 7.0 Hz), 4.80 (s, 2H), 5.05 (m, 2H), and 5.75 (m, 1H).

To a solution containing 0.50 g (2.1 mmol) of the above compound and 0.49 g (2.1 mmol) of *p*-acetamidobenzenesulfonylazide in 7 mL of acetonitrile was added 5.14 mmol of Et_3N at 0 °C. The solution was stirred at 0 °C for 1 h and at 25 °C for 2 h. The solvent was removed under reduced pressure, and the resulting residue was taken up in 5 mL of CH_2Cl_2. After filtration, the solvent was removed under reduced pressure and the crude product was purified by flash silica gel chromatography to give 320 mg (60%) of ethyl 2-oxo-6-heptenyl diazomalonate (**14**) as a light yellow oil: IR (neat) 2135, 1765, 1735, 1700, 1380, and 1335 cm^{-1}; ^1H-NMR ($CDCl_3$, 90 MHz) δ 1.32 (t, 3H, J = 7.0 Hz), 1.75 (m, 2H), 2.00 (m, 2H), 2.48 (t, 2H, J = 7.2 Hz), 4.35 (q, 2H, J = 7.0 Hz), 4.82 (s, 2H), 5.05 (m, 2H), and 5.80 (m, 1H).

A solution containing 60 mg (0.22 mmol) of diazomalonate **14** in 3 mL of benzene was treated with a catalytic amount of rhodium(II) acetate. The solution was placed in a 90 °C preheated oil bath and was heated until N_2 evolution had ceased (*ca.* 30 min). After being cooled to rt, the solution was filtered through a pad of Celite and the solvent was removed under reduced pressure. The resulting residue was subjected to flash silica gel chromatography to give 35 mg (67%) of ethyl decahydro-1*H*-7-carboxy-3a,7-epoxy-5-oxaazulene-6-one (**16**) as a clear oil: IR (neat) 1775, 1760, 1470, 1330, and 1245 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.32 (t, 3H, J = 7.1 Hz), 1.53 (m, 2H), 1.75 (m, 1H), 1.96 (m, 2H), 2.05 (m, 1H), 2.24 (dd, 1H, J = 12.6 and 5.9 Hz), 2.70 (m, 1H), 2.78 (dd, 1H, J = 12.6 and 9.1 Hz), 4.16 (d, 1H, J = 10.6 Hz), 4.32 (m, 2H) and 4.69 (d, 1H, J = 10.6 Hz). Anal. Calcd for $C_{12}H_{16}O_5$: C, 59.98; H, 6.72. Found: C, 59.83; H, 6.54.

Preparation and Rhodium(II) Acetate Catalyzed Reaction of 2-Propenyl 2-Oxo-2-phenylethyl Diazomalonate (15). A solution containing 1.0 g (7.3 mmol) of 2-hydroxyacetophenone and 1.26 g (8.7 mmol) of 2-propenyl hydrogen malonate in 15 mL of CH_2Cl_2 was treated with 1.67 g (8.1 mmol) of dicyclohexylcarbodiimide and 0.10 g (0.8 mmol) of 4-(dimethylamino)pyridine at 0 °C. The solution was allowed to warm to rt and was further stirred for an additional 15 h. The mixture was filtered in order to remove dicyclohexylurea, and the filtrate was concentrated under reduced pressure. The resulting residue was subjected to flash chromatography to give 0.4 g (23%) of 2-propenyl 2-oxo-2-phenylethyl malonate as a clear oil: IR (neat) 1765, 1745, 1705, 1460, 1380, and 1160 cm^{-1}; ^1H-NMR ($CDCl_3$, 90 MHz) δ 3.60 (s, 2H), 4.70 (m, 2H), 5.75 (m, 1H), and 7.80 (m, 5H).

To a solution containing 163 mg (0.62 mmol) of the above compound and 156 mg (0.65 mmol) of *p*-acetamidobenzenesulfonyl azide in 3 mL of acetonitrile was added 0.22 mL (1.58 mmol) of Et_3N at 0 °C. The solution was allowed to warm to rt and was further stirred for 2 h. The mixture was concentrated under reduced pressure, and the residue was taken up in 5 mL of CH_2Cl_2. After filtration, the crude product was purified by flash silica gel chromatography to give 120 mg (67%) of 2-propenyl 2-oxo-2-phenylethyl diazomalonate (**15**) as a yellow oil: IR (neat) 2160, 1770, 1755, 1710, 1385, 1350, and 1110 cm^{-1}; ^1H-NMR ($CDCl_3$, 90 MHz) δ 3.25 (s, 2H), 4.80 (d, 2H, J = 6.0 Hz), 5.32 (m, 2H), 5.50 (s, 2H), 5.85 (m, 1H), and 7.80 (m, 5H).

A solution containing 40 mg (0.14 mmol) of **15** and 27 mg (0.16 mmol) of *N*-phenylmaleimide in 1.5 mL of benzene was treated with a catalytic amount of rhodium(II) acetate. The solution was placed in a 90 °C preheated oil bath and was heated until N_2 evolution had ceased (*ca.* 20 min). After being cooled to rt, the solution was filtered through a pad of Celite and the solvent was removed under reduced pressure. The crude solid was recrystallized from CH_2Cl_2–hexane to give 36 mg (58%) of the expected bimolecular dipolar cycloadduct **17** as a white solid: mp 182–183 °C; IR (KBr) 1780, 1735, 1510, 1390, 1300, and 1215 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 3.95 (d, 1H, J = 7.4 Hz), 4.32 (d, 1H, J = 7.4 Hz), 4.67 (d, 1H, J = 11.2 Hz), 4.85 (d, 1H, J = 11.2 Hz), 4.97 (d, 1H, J = 5.8 Hz), 5.32 (dd, 1 H, J = 12.8 and 1.2 Hz), 5.50 (dd, 1H, J = 12.8 and 1.2 Hz), 6.21 (m, 1H), and 7.35 (m, 10H). Anal. Calcd for $C_{24}H_{19}NO_7$: C, 66.49; H, 4.42; N, 3.23. Found: C, 66.25; H, 4.27; N, 3.04.

Rhodium(II) Acetate Catalyzed Reaction of 2-Butynyl Diazoacetate (24). A sample of 2-butynyl 2-diazo-3-oxobutanoate (**22**) was prepared from 2-butyn-1-ol in the normal manner[40] in 72% yield: IR (neat) 2150, 1725, 1655, 1310, 1060, 965, and 740 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz), δ 1.83 (t, 3H, J = 2.1 Hz), 2.44 (s, 3H), and 4.76 (q, 2H, J = 2.1 Hz). This diazo compounds was converted with Rh(II) acetate into 1-oxo-4,6-dimethyl-1*H*,3*H*-furo[3,4-*c*]furan (**23**) (75%): mp 74–75 °C; IR (KBr) 1770, 1630, 1380, 1270, 1185, 1035, and 975 cm^{-1}; ^1H-NMR ($CDCl_3$, 360 MHz) δ 2.19 (s, 3H), 2.38 (s, 3H), and 5.00 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 12.2, 12.3, 64.0, 114.2, 124.4, 139.5, 149.4, and 165.5; *m/e* 152 (M^+) base, 122, 109, 81 and 65. Anal. Calcd for $C_8H_8O_3$: 63.14; H, 5.30. Found: C, 63.02; H, 5.14.

A sample of 2-butynyl diazoacetate (**24**) was prepared from **22** by deacylation with pyrrolidine. To a stirred solution containing 1.0 g (7.2 mmol) of **24** in 100 mL of dry benzene was added 20 mg of rhodium(II) acetate. The solution was heated at reflux for 3 h and was then concentrated under reduced pressure. The resulting oil was purified to give 570 mg (42%) of 2-butynyl cycloheptatrienecarboxylate (**25**): IR (neat) 1740, 1437, 1263, and 1160 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.82 (t, 3H, J = 2 Hz), 2.57 (m, 1H), 4.66 (q, 2H, J = 2 Hz), 5.40 (m, 2H), 6.23 (m, 2H), and 6.65 (m, 2H). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.56; H, 5.43. Found: C, 76.41; H, 5.09.

The minor product isolated from the silica gel column (160 mg, 10%) corresponded to a 3:1 mixture of di-2-butynyl fumarate (**26a**) and di-2-butynyl maleate (**26b**). Compound **26a**: IR ($CHCl_3$) 1715, 1665, 1440, 1305, and 1160 cm^{-1}; ^1H-NMR ($CDCl_3$, 90 MHz) δ 1.92 (t, 6H, J = 2 Hz), 4.85 (q, 4H, J = 2 Hz), and 6.91 (s, 2H). Compound **26b**: IR ($CHCl_3$) 1710, 1665, 1445, 1295, and 1170 cm^{-1}; ^1H-NMR ($CDCl_3$, 90 MHz) δ 1.92 (t, 6H, J = 2 Hz), 4.85 (q, 4H, J = 2 Hz), and 6.21 (s, 2H). Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.43; H, 5.50. Found: C, 65.27; H, 5.36.

Preparation and Rhodium(II)-Catalyzed Reaction of Oct-7-en-2-ynyl 2-Diazo-3-oxobutanoate (27). To a solution containing 1.0 g (8.1 mmol) of oct-7-en-2-yn-1-ol in 25 mL of distilled THF at 0 °C was added dropwise 0.75 mL (9.7 mmol) of diketene. The resulting yellow solution was allowed to warm to 25 °C and was stirred for an addition 2 h. Removal of the solvent under reduced pressure left an orange oil which was taken up in 30 mL of benzene. To this solution was added 0.98 g (12.2 mmol) of mesyl azide and 3 mL of triethylamine. The resulting mixture was stirred at 25 °C for 16 h. Concentration of the mixture under reduced pressure afforded an oil which chromatographed on silica gel to give 1.25 g (66%) of **27**: IR (neat) 2142, 1719, 1366, and 1312 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 1.63 (quin, 2H, J = 7.4 Hz), 2.13 (q, 2H, J = 7.4 Hz), 2.24 (tt, 2H, J = 7.3 and 2.1 Hz), 2.48 (s, 3H), 4.82 (t, 2H, J = 2.1 Hz), 4.96–5.05 (m, 2H), and 5.70–5.85 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.1, 27.4, 28.2, 32.7, 53.4, 73.6, 88.1, 115.3, 137.5, 160.8, and 189.8.

A solution containing 0.15 g (0.64 mmol) of **27** in 25 mL of benzene under N_2 was treated with 5 mg of rhodium(II) octanoate and was then heated at reflux for 25 min. Concentration of the mixture under reduced pressure left a green oil which was chromatographed on silica gel to give 102 mg (77%) of furan **28**:

IR (neat) 2935, 1773, 1625, and 1351 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.65 (quin, 2H, J = 7.5 Hz), 2.05 (q, 2H, J = 7.2 Hz), 2.39 (s, 3H), 2.56 (t, 2H, J = 7.5 Hz), 4.92–5.00 (m, 2H), 5.04 (s, 2H), and 5.68–5.74 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 12.9, 26.3, 26.4, 33.0, 64.8, 114.8, 115.4, 124.8, 137.5, 144.1, 150.0, and 165.0; HRMS calcd for $C_{12}H_{14}O_3$ 206.0943, found 206.0943.

Preparation and Rhodium(II)-Catalyzed Reaction of Oct-7-en-2-ynyl 2-Diazoacetate (29). To a flask charged with 0.30 g (1.3 mmol) of **27** was added 4 mL of distilled pyrrolidine. The resulting yellow solution was stirred at 25 °C for 2 h. Removal of the excess pyrrolidine under reduced pressure was followed by silica gel chromatography to give 0.21 g (84%) of **29**: IR (neat) 2238, 2113, and 1700 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.61 (quin, 2H, J = 7.6 Hz), 2.14 (q, 2H, J = 7.6 Hz), 2.24 (tt, 2H, J = 7.6 and 2.2 Hz), 4.76 (t, 2H, J = 2.2 Hz), 4.80 (s, 1H), 4.97–5.05 (m, 2H), and 5.73–5.84 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.1, 27.5, 32.7, 46.3, 53.0, 74.2, 87.4, 115.2, and 137.6.

To a solution containing 150 mg of **29** in 25 mL of benzene was added 3 mg of $Rh_2(OAc)_4$, and the resulting solution was heated at reflux for 30 min. Concentration of the mixture under reduced pressure left an oil which was purified by silica gel chromatography to give 150 mg (79%) of oct-7-en-2-ynyl 2,4,6-cycloheptatrienylacetate (**30**): IR (neat) 2238, 1744, and 1374 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.56–1.68 (m, 2H), 2.10–2.19 (m, 2H), 2.23 (tt, 2H, J = 7.0 and 2.0 Hz), 2.55–2.60 (m, 1H), 4.79 (t, 2H, J = 1.8 Hz), 4.95–5.08 (m, 2H), 5.40–5.48 (m, 2H), 6.25–6.30 (m, 2H), and 6.62–6.68 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.2, 27.5, 32.7, 43.7, 53.4, 74.1, 87.5, 115.3, 116.2, 125.7, 130.9, 137.6, and 172.4; HRMS calcd for $C_{16}H_{18}O_2$ 242.1306, found 242.1306.

Preparation and Rhodium(II)-Catalyzed Reaction of *N*-Benzyl-*N*-oct-7-en-2-ynyl-2-diazo-3-oxobutanamide (31). A solution containing 3 mL (28 mmol) of benzylamine and 6 mL (26 mmol) of di-*tert*-butyl dicarbonate in 25 mL of 1,4-dioxane was heated at 90 °C for 4 h. Removel of the dioxane under reduced pressure left an oil which was chromatographed on silica gel to give 5.2 g (96%) of *N*-benzyl-*N*-(*tert*-butyloxycarbonyl)amine: mp 54–55 °C; IR ($CHCl_3$) 2981, 1679, 1455, and 1366 cm^{-1}; ^{1}H-NMR (90 MHz, $CDCl_3$) δ 1.46 (s, 9H), 4.31 (d, 2H, J = 6.9 Hz), 4.82 (s, 1H), and 7.25-7.33 (m, 5H).

To a flask charged with 1.0 g (4.8 mmol) of the above amine in 20 mL of a 1:1 mixture of THF–DMF solution at 0 °C was added, in one portion, 0.29 g (7.2 mmol) of NaH (60% dispersion in mineral oil). The resulting mixture was allowed to warm to 25 °C and was stirred at rt for 40 min. To this mixture was added 1.1 g (5.8 mmol) of 1-bromo-oct-7-en-2-yne. The yellow suspension was stirred at 25 °C for 3 h, and the mixture was extracted with ether and washed with water and brine. Concentration of the solution under reduced pressure left a yellow oil, which on silica gel chromatography gave 1.3 g (86%) of *N*-benzyl-*N*-(*tert*-butyloxycarbonyl)-*N*-oct-7-en-2-ynylamine. A solution containing 1.0 g (3.2 mmol) of this product in 10 mL of ethyl acetate was treated with 5 mL of concentrated HCl at 25 °C. The initially formed suspension became clear after 15 min. Stirring was maintained for another 30 min, and the mixture was added to 50 mL of ether. A saturated sodium bicarbonate solution was used to neutralize the acidity. The organic phase was washed with brine, dried over KCO_3, and concentrated under reduced pressure. Chromatography of the crude oil on silica gel gave 0.37 g (54%) of *N*-benzyl-*N*-oct-7-en-2-ynylamine: IR (neat) 1642, 1455, and 1329 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.62 (quin, 2H, J = 7.3 Hz), 2.14–2.26 (m, 4H), 3.40 (s, 2H), 3.86 (s, 2H), 4.97–5.08 (m, 2H), 5.76–5.85 (m, 1H), and 7.24–7.35 (m, 5H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.2, 28.1, 32.8, 37.9, 52.5, 78.2, 83.5, 115.1, 127.0, 128.4, 137.9, and 139.7.

To a flask charged with 0.50 g (2.3 mmol) of the above amine in 15 mL of distilled THF at 0 °C under N_2 was added dropwise 0.25 mL (3.2 mmol) of diketene. The resulting yellow solution was allowed to warm to 25 °C and was stirred at rt for 2 h. Removal of the solvent under reduced pressure left an orange oil which was taken up in 20 mL of benzene. To this solution was added 0.39 g (3.2 mmol) of mesyl azide and 3 mL of triethylamine. The mixture was stirred at 25 °C for 16 h. Concentration of the solution under reduced pressure gave an oil which was chromatographed on silica gel to give 0.47 g (63%) of *N*-benzyl-*N*-oct-7-en-2-ynyl-2-diazo-3-oxobutanamide (**31**): IR (neat) 2105, 1654, 1420, and 1289 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.58 (quin, 2H, J = 7.3 Hz), 2.11 (q, 2H, J = 7.3 Hz), 2.19 (tt, 2H, J = 7.3 and 2.1 Hz), 2.35 (s, 3H), 4.00 (t, 2H, J = 2.1 Hz), 4.67 (s, 2H), 4.96–5.05 (m, 2H), 5.72–5.78 (m, 1H), and 7.25–7.33 (m, 5H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.0, 27.4, 27.7, 32.7, 37.6, 49.9, 73.7, 85.7, 115.3, 127.8, 127.9, 128.8, 135.7, 137.6, and 161.4.

A solution containing 120 mg (0.37 mmol) of **31** in 20 mL of benzene was treated with 5 mg of Rh(II) octanoate under N_2. The resulting solution was heated at reflux for 1 h, and the solution was concentrated under reduced pressure to give a green oil. The crude oil when chromatographed on silica gel gave 91 mg (83%) of furan **32**: IR (neat) 2925, 1766, 1694, and 1409 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.68 (quin, 2H, J = 7.2 Hz), 2.09 (q, 2H, J = 7.2 Hz), 2.47 (s, 3H), 2.54 (t, 2H, J = 7.3 Hz), 4.03 (s, 2H), 4.62 (s, 2H), 4.95–5.02 (m, 2H), 5.69–5.82 (m, 1H), and 7.24–7.40 (m, 5 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 12.8, 26.5, 33.2, 43.9, 46.7, 115.2, 119.6, 119.9, 127.5, 128.2, 128.7, 137.1, 137.8, 144.3, 146.2, and 164.2; HRMS calcd for $C_{19}H_{21}NO_2$ 295.1572, found 295.1570.

Preparation and Rhodium(II)-Catalyzed Reaction of *N*-Benzyl-*N*-oct-7-en-2-ynyl-2-diazoacetamide (33). To a flask charged with 0.10 g (0.31 mmol) of diazoamide **31** was added 3 mL of distilled pyrrolidine. The resulting yellow solution was stirred at 25 °C for 2 h. Removal of the excess pyrrolidine under reduced pressure followed by chromatography on silica gel gave 81 mg (93%) of diazoamide **33**: IR (neat) 2935, 2107, 1617, and 1430 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.56 (quin, 2H, J = 7.3 Hz), 2.07–2.21 (m, 4H), 4.00 (brs, 2H), 4.56 (s, 2H), 4.96–5.07 (m, 3H), 5.70–5.84 (m, 1H), and 7.24–7.36 (m, 5H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.0, 27.7, 32.7, 36.1, 47.0, 49.5, 74.7, 84.7, 115.2, 127.4, 127.6, 128.7, 136.7, 137.7, and 166.1.

A solution containing 0.15 g (0.53 mmol) of **33** in 25 mL of benzene under N_2 was treated with 5 mg of rhodium(II) octanoate. The resulting solution was heated at reflux for 45 min and then concentrated under reduced pressure. The crude oil obtained was chromatographed on silica gel to give 55 mg (41%) of the cyclopropanation product **34**, as well as 44 mg (33%) of cycloheptatriene **35**. Compound **34** showed the following spectral properties: IR ($CHCl_3$) 2943, 1669, 1445, and 1237 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.75 (dd, 1H, J = 8.3 and 5.4 Hz), 0.89–0.96 (m, 1H), 1.17–1.35 (m, 1H), 1.46–1.52 (m, 1H), 1.62–1.93 (m, 5H), 3.54 (d, 1H, J = 18.5 Hz), 3.65 (d, 1H, J = 18.5 Hz), 4.57 (s, 2H), 5.87 (s, 1H), and 7.20–7.34 (m, 5H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 16.8, 20.4, 27.3, 29.4, 29.5, 29.8, 45.8, 52.0, 118.8, 127.4, 127.9, 128.7, 137.6, 163.8, and 172.2; HRMS calcd for $C_{17}H_{19}NO$ 253.1467, found 253.1467. Compound **35** showed the following properties: IR (neat) 3022, 2937, 1700, 1426, and 1273 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.57–1.63 (m, 2H), 2.10–2.23 (m, 4H), 3.11 (brs, 1H), 4.12–4.30 (m, 4H), 4.96–5.06 (m, 2H), 5.25–5.29 (m, 1H), 5.73–5.82 (m, 1H), 6.16–6.21 (m, 2H), 6.48–6.50 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.0, 27.7, 32.3, 32.8, 46.3, 50.3, 73.5, 84.7, 115.2, 199.6, 120.4, 126.9, 129.0, 129.9, 130.3, 137.6, and 173.4; HRMS calcd for $C_{17}H_{19}NO$ 253.1467, found 253.1467.

Preparation and Rhodium(II)-Catalyzed Reaction of *N*-Methyl-*N*-[1-(phenylethynyl)but-3-enyl]-2-diazoacetamide (37). To a suspension containing 410 mg (16.9 mmol) of magnesium turnings in 20 mL of ether was added a solution of 2.04 g (16.9 mmol) of allyl bromide in 10 mL of ether at a rate as to maintain gentle reflux. The reaction mixture was heated at reflux for a further 3 h and then cooled to 0 °C. A 2.0-g (15.3 mmol) sample of phenylpropargyl aldehyde in 10 mL of ether was added dropwise, and the reaction mixture was stirred for a further 2 h at rt. The mixture was quenched with water and the organic layer separated. Removal of the solvent under reduced pressure left an oil which was chromatographed on silica gel to give 1.9 g (71%) of 1-(phenylethynyl)but-3-en-1-ol; IR (neat) 2229, 1639, and 1433 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.58 (m, 2H), 2.76 (d, 1H, J = 6.0 Hz), 4.66 (dt, 1H, J = 6.2 and 6.0 Hz), 5.22 (m, 2H), 5.96 (m, 1H), and 7.25-7.47 (m, 5H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 42.2, 62.1, 85.2, 89.6, 118.9, 122.6, 128.3, 128.4, 131.7, and 133.2.

To a flask charged with 1.5 g (8.7 mmol) of the above alcohol in 70 mL of THF at 0 °C was added 2.5 g (9.5 mmol) of triphenylphosphine, 1.4 g (9.5 mmol) of phthalimide, and 1.7 mL (10.8 mmol) of DEAD. The resulting mixture was allowed to warm to 25 °C and was stirred at rt for 8 h. Concentration of the solution under reduced pressure left a viscous orange oil, which on silica gel chromatography gave 1.5 g (56%) of

N-[1-(phenylethynyl)but-3-enyl]phthalimide: IR (neat) 2920, 1710, 1395, 1345, and 1120 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 2.92–3.01 (m, 2H), 5.13 (m, 2H), 5.31 (t, 1H, J = 6.2 Hz), 5.78 (m, 1H), 7.26–7.29 (m, 3H), 7.31–7.44 (m, 2H), 7.68–7.75 (m, 2H), and 7.82–7.88 (m, 2H).

A solution containing 1.5 g (4.9 mmol) of the above product in 50 mL of ethyl alcohol was treated with 0.3 mL of 85% hydrazine hydrate in water, and the solution was heated at reflux for 3.5 h. Upon cooling a white precipitate formed. Concentrated HCl (6 mL) was added to the mixture, the precipitate was filtered, and the volatiles were removed under reduced pressure. The resulting yellow solid was dissolved in 60 mL of a 2:1 ethyl alcohol–water mixture and rendered basic by the addition of 1 N NaOH. Repeated extraction of the aqueous phase using ether, followed by drying of the organic extracts ($MgSO_4$) and removal of the solvent under reduced pressure, gave 0.78 g (93%) of 1-(phenylethynyl)but-3-en-1-amine which was used in the next step without further purification: IR (neat) 2219, 1638, and 1440 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 2.58 (m, 2H), 2.76 (d, 1H, J = 6.0 Hz), 4.66 (dt, 1H, J = 6.2 and 6.0 Hz), 5.22 (m, 2H), 5.96 (m, 1H), and 7.25–7.47 (m, 5H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 42.4, 43.5, 82.8, 92.2, 118.3, 123.2, 128.0, 128.2, 131.6, and 134.1.

A 0.74-g (4.6 mmol) sample of the above amine was dissolved in 4 mL of 1,4-dioxane, 1.0 g (4.6 mmol) of di-*tert*-butyl dicarbonate was added, and the reaction mixture was heated at 90 °C for 4 h. Removal of the dioxane under reduced pressure left a yellow oil which was used in the next step without further purification. A solution containing 1.2 g (4.6 mmol) of the above carbamate in 10 mL of THF was cooled to 0 °C, and 3.1 mL of a 1.6 M *n*-butyllithium solution in hexane (5.0 mmol) was added dropwise. The reaction mixture was stirred at this temperature for 30 min before 0.65 g (4.6 mmol) of methyl iodide was added. After the mixture was warmed to rt over 1 h, 1 mL of water was added and the aqueous layer was extracted with EtOAc. The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The resulting yellow oil was dissolved in 10 mL of THF, and 2 mL of concentrated HCl was added. After being stirred for 1 h, the reaction was heated at reflux for a further 3 h, cooled to rt, and poured into 10 mL of water. Neutralization with solid Na_2CO_3 was followed by extraction with EtOAc, and removal of the solvent under reduced pressure gave 0.39 g (48%) of a brown oil. Attempts to purify this compound led to decomposition so it was used directly in the next step. A solution of 0.39 g (2.1 mmol) of this compound in 15 mL of THF at 0 °C was treated with 0.23 mL (2.9 mmol) of diketene. The solution was warmed to rt and was stirred for 3 h. The volatiles were removed under reduced pressure, and the residue was dissolved in 10 mL of benzene. A 0.35-mg (2.9 mmol) sample of mesyl azide was added followed by 0.42 mL (3.0 mmol) of Et_3N, and the reaction mixture was stirred at rt for 12 h. Concentration of the solution under reduced pressure left an oil which was chromatographed on silica gel to give 0.56 g (91%) of *N*-methyl-*N*-[1-(phenylethynyl)but-3-enyl]-2-diazo-3-oxobutylamide: IR (neat) 2108, 1748, 1642, 1381, 1263, and 1033 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H), 2.58 (m, 2H), 3.06 (s, 3H), 5.21 (m, 2H), 5.35 (m, 1H), 5.80 (m, 1H), 7.30 (m, 3H), and 7.43 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 27.4, 27.8, 38.2, 39.8, 77.2, 85.5, 118.7, 128.3, 128.6, 129.0, 131.8, 132.9, and 161.4.

A 25-mL flash was charged with 458 mg (1.5 mmol) of *N*-methyl-*N*-[1′-(phenylethynyl)but-3-enyl]-2-diazo-3-oxobutylamide and 10 mL (120 mmol) of pyrolidine, and the reaction mixture was stirred at rt for 2 h. The excess pyrolidine was removed under reduced pressure, and the residue was purified by silica gel chromatography to give 273 mg (68%) of *N*-methyl-*N*-[1-(phenylethynyl)but-3-enyl]-2-diazoacetamide (**37**) as a bright yellow oil: IR (neat) 2108, 1607, 1436, 1398, and 1189 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 2.51 (m, 2H), 2.89 (s, 3H), 4.99 (s, 1H), 5.15 (m, 2H), 5.65 (bs, 1H), 5.81 (ddt, 1H, J = 17.0, 10.1 and 7.0 Hz), and 7.27–7.48 (m, 5H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 30.0, 38.5, 46.6, 84.9, 86.5, 118.3, 122.5, 128.3, 128.5, 131.7, 133.4, and 165.7.

A 30-mg (0.12 mmol) sample of the above diazo compound was dissolved in 25 mL of benzene, and 2 mg of rhodium(II) octanoate was added. The mixture was stirred at rt for 3 h. Removal of the volatiles under reduced pressure left an oil which was chromatographed on silica gel to give 20 mg (65%) of **39**: IR (neat) 2222, 1631, 1438, and 1393 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 2.52 (m, 3H), 3.27 (s, 3H), 5.12 (m, 2H), 5.88 (m, 2H), and 7.27–7.45 (m, 5H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 31.5, 38.3, 39.8, 46.6, 85.3, 86.4, 188.3, 128.1, 128.2, 131.5, 131.7, 133.1, and 164.8; HRMS calcd for $C_{15}H_{15}NO$ 225.1154, found 225.1154.

Preparation and Rhodium(II)-Catalyzed Reaction of *N*-Methyl-*N*-oct-7-en-2-ynyl-2-diazo-3-oxobutanamide (36). To a flask containing 2.0 g (16.1 mmol) of oct-7-en-2-yn-1-ol[55] in 75 mL of THF at °C was added 4.5 g (17.1 mmol) of triphenylphosphine, 2.7 g (18.3 mmol) of phthalimide, and 3.1 mL (19.1 mmol) of DEAD. The resulting mixture was allowed to warm to 25 °C and was stirred at rt for 8 h. Concentration of the solution under reduced pressure left a yellow oil, which was purified by silica gel chromatography to give 2.1 g (51%) of *N*-oct-7-en-2-ynylphthalimide as a white solid: mp 33–34 °C; IR (neat) 2135, 1695, 1610, and 1380 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 1.53 (m, 2H), 2.10 (m, 4H), 4.39 (t, 2H, J = 2.2 Hz), 4.94 (m, 2H), 5.71 (ddt, 1H, J = 17.1, 10.1 and 6.7 Hz), 7.69 (dd, 2H, J = 5.4 and 3.1 Hz) and 7.83 (dd, 2H, J = 5.4 and 3.1 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.0, 27.5, 32.7, 51.3, 73.7, 83.3, 115.1, 123.4, 132.1, 134.0, 137.7, and 167.2.

A solution containing 1.25 g (4.9 mmol) of the above product in 30 mL of ethyl alcohol was treated with 0.17 of 85% hydrazine hydrate in water, and the reaction mixture was heated at reflux for 3.5 h. Upon cooling a white precipitate formed. Addition of 6 mL of concentrated HCl followed by filtration and removal of the volatiles under reduced pressure left a white solid. This compound was dissolved in 60 mL of a 2:1 mixture of ethyl alcohol and water and was rendered basic by addition of 1 N NaOH. Repeated extraction of the aqueous phase using ether, drying of the organic extracts ($MgSO_4$), and removal of the solvent under reduced pressure gave 0.51 g (84%) of oct-7-en-2-ynylamine which was used in the next step without further purification: IR (neat) 2215, 1610, and 1380 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 1.57 (m, 2H), 2.13 (m, 4H), 3.38 (bs, 2H), 4.65 (bs, 2H), 4.98 (m, 2H), and 5.76 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.1, 27.9, 32.8, 58.3, 82.4, 115.1, and 137.9.

A 1.0 g (8.1 mmol) sample of the above amine was dissolved in 7 mL of 1,4-dioxane, and 1.8 g (8.1 mmol) of di-*tert*-butyldicarbonate was added. The reaction mixture was heated at 90 °C for 4 h. Removal of the dioxane under reduced pressure followed by silica gel chromatography afforded 1.3 g (84%) of *N*-oct-7-en-2-ynyl-*N*-(*tert*-butyloxycarbonyl)amine as a viscous clear oil: IR (neat) 2210, 1690, 1485, 1350, and 1140 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 1.47 (s, 9H), 1.55 (m, 2H), 2.06 (m, 4H), 3.80 (bs, 1H), 4.88–4.92 (m, 2H), 4.99 (m, 2H), and 5.76 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 17.9, 27.3, 27.9, 28.3, 33.2, 76.3, 85.0, 115.3, 137.7, and 163.6.

A solution of 1.1 g (4.9 mmol) of the above carbamate in 10 mL of THF was cooled to −78 °C, and 3.3 mL of a 1.6 M solution of *n*-butyllithium in hexane (5.3 mmol) was added dropwise. The mixture was stirred at this temperature for 30 min before 0.76 g (5.3 mmol) of methyl iodide was added. After the mixture was warmed to rt over 1 h, 1 mL of water was added, and the aqueous layer was extracted with EtOAc. The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The resulting yellow oil was dissolved in 10 mL of EtOAc, and 1 mL of concentrated HCl was added. After being stirred for 1 h, the reaction was poured into 10 mL of water and was rendered neutral with solid sodium carbonate, and the aqueous layer was extracted several times with EtOAc. Removal of the solvent afforded 0.16 g (24%) of a brown oil which due to its unstable nature was used immediately in the next step. A 0.16-g (1.2 mmol) sample of the oil was dissolved in 10 mL of THF, and the reaction was cooled to 0 °C. A 0.19-mL (2.4 mmol) sample of diketene was added dropwise, and the mixture was stirred at rt for 2 h. The volatiles were removed under reduced pressure, and the residue was dissolved in 10 mL of benzene. A 0.16-g (1.3 mmol) sample of mesyl azide was added followed by 0.29 g (3.0 mmol) of Et_3N, and the mixture was stirred at rt for 8 h. Evaporation of the solvent and subsequent silica gel chromatography afforded 0.16 g (56%) of *N*-methyl-*N*-oct-7-en-2-ynyl-2-diazo-3-oxobutylamide (**36**) as a yellow oil: IR (neat) 2105, 1710, and 1635 cm^{-1}; ^1H-

(55) Bulman-Page, P. C.; Rayner, C. M.; Sutherfield, I. O. *J. Chem. Soc., Chem. Commun.* **1988**, 356.

NMR (300 MHz, $CDCl_3$) δ 1.49 (m, 2H), 2.00–2.34 (m, 4H), 2.35 (s, 3H), 2.93 (s, 3H), 4.10 (bs, 2H), 4.89 (m, 2H), and 5.67 (ddt, 1H, J = 17.0, 6.8 and 3.4 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.0, 27.6, 27.7, 32.7, 50.1, 74.4, 84.2, 86.9, 115.2, 137.5, 166.4, and 202.1.

A 42-mg (0.17 mmol) sample of diazoamide **36** was dissolved in 9.2 mL of benzene, and a catalytic amount of rhodium(II) octanoate was added. The reaction mixture was heated at reflux for 2 h. Removal of the solvent and subsequent purification of the residue by silica gel chromatography gave 27 mg (72%) of furan **41** as a clear oil: IR (neat) 1695, 1647, 1496, and 1342 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.63 (m, 2H), 2.08 (m, 4H), 2.45 (t, 2H, J = 8.1 Hz), 2.53 (s, 3H), 3.51 (s, 3H), 5.00 (m, 2H), and 5.76 (m, 1H), 6.06 (d, 1H, J = 7.0 Hz), and 7.24 (d, 1H, J = 7.0 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 21.0, 29.4, 32.5, 33.4, 37.4, 46.6, 108.2, 115.1, 115.3, 137.8, 138.3, 117.4, and 151.9; HRMS calcd for $C_{13}H_{17}NO_2$ 219.1259, found 219.1259.

Preparation and Rhodium(II)-Catalyzed Reaction of *N*-Methyl-*N*-oct-7-en-2-ynyl-2-diazoacetamide (38). To a flask containing 0.41 g (1.65 mmol) of diazoamide **36** in 10 mL of CH_2Cl_2 was added 2 mL of pyrrolidine. The resulting yellow solution was stirred at 0 °C for 1 h and then at 25 °C for a further 8 h. Removal of the solvent under reduced pressure followed by silica gel chromatography gave 0.28 g (82%) of diazoamide **38**: IR (neat) 2921, 2099, 1614, and 1399 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.47 (m, 2H), 2.03-2.09 (m, 4H), 2.82 (s, 3H), 4.04 (brs, 2H), 4.88 (m, 2H), 5.01 (s, 1H), and 5.65 (ddt, 1H, J = 17.0, 10.2, and 6.7 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 17.9, 27.6, 32.6, 33.6, 37.5, 46.4, 74.5, 84.2, 115.1, 137.6, and 165.7.

A solution containing 42 mg (0.20 mmol) of **38** in 20 mL of benzene under N_2 was treated with 5 mg of rhodium(II) octanoate. The resulting solution was immersed in a preheated oil bath, heated at reflux for 1 h, and then concentrated under reduced pressure. The resulting crude oil was chromatographed on silica gel to give 21 mg (58%) of bicyclo[3.1.0]hexane **40**: IR (neat) 2930, 1676, 1446, and 1239 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.81 (dd, 1H, J = 8.3 and 5.4 Hz), 0.93 (m, 1H), 1.26 (m, 1H), 1.48–1.55 (m, 1H), 1.62–1.93 (m, 5H), 2.97 (s, 3H), 3.68 (d, 1H, J = 18.0 Hz), 3.72 (d, 1H, J = 18.0 Hz), and 5.83 (s, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.0, 20.5, 27.6, 29.4, 29.6, 29.9, 30.2, 55.7, 119.6, 163.2, and 172.7; HRMS calcd for $C_{11}H_{15}NO$ 177.1154, found 177.1157.

Preparation and Rhodium-Catalyzed Decomposition of *N*-(2-Diazo-1,3-oxobutyl)-1-(phenylethynyl)pyrrolidine (42). To a solution of 5.0 g (58.8 mmol) of 2-pyrrolidinone in 120 mL of CH_2Cl_2 was added 7.2 g (58.8 mmol) of DMAP, 8.2 mL (58.8 mmol) of Et_3N, and 15.3 g (70.6 mmol) of di-*tert*-butyl dicarbonate, and the mixture was stirred at rt for 8 h. After this time the solution was poured into 50 mL of a saturated copper sulfate solution and extracted with ether. The combined extracts were washed with water and dried over $MgSO_4$. Removal of the solvent under reduced pressure was followed by silica gel chromatography to give 8.81 g (81%) of N-(*tert*-butyloxycarbonyl)-2-pyrrolidinone: IR (neat) 1780, 1745, 1705, 1310, and 1155 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.47 (s, 9H), 1.94 (m, 2H), 2.46 (m, 2H), and 3.70 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 17.3, 27.8, 32.8, 46.3, 82.4, 150.0, and 174.3.

To a solution of 0.92 g (9.0 mmol) of phenylacetylene in 9 mL of THF was added 5.6 mL of a 1.6 M *n*-butyllithium solution in hexane (9.0 mmol), and the mixture was stirred at −78 °C for 10 min. After this time 1.2 mL (9.8 mmol) of boron trifluoride etherate was added, and the solution was stirred for a further 10 min. A 0.56-g (3.0 mmol) sample of the above carbamate was added dropwise as a solution in 6 mL of THF, and the mixture was stirred for 1 h. The solution was quenched with 2 mL of methanol, and 0.38 g (10.0 mmol) of sodium borohydride was added. After the solution was warmed to rt over 8 h, the solvent was removed under reduced pressure, the residue was dissolved in 10 mL of EtOAc, 1 mL of concentrated HCl was cautiously added, and the mixture was stirred at rt for 3 h. Addition of 10 mL of water was followed by neutralization with solid sodium carbonate and extraction using CH_2Cl_2 to afford a bright yellow oil after removal of the solvent. Silica gel chromatography of the residue gave 0.34 g (65%) of 1-(phenylethynyl)pyrrolidine: IR (neat) 1590, 1478, and 1060 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.72–2.08 (m, 4H), 2.88 (ddd, 1H, J = 10.4, 7.7, and 5.4 Hz), 3.09 (m, 1H), 3.98 (dd, 1H, J = 7.1 and 5.2 Hz), 7.25 (m, 3H), and 7.36 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 24.9, 33.3, 46.2, 49.3, 82.3, 91.7, 123.3, 127.9, 128.2, and 131.6.

A solution of 164 mg (0.96 mmol) of the above amine in 7 mL of THF was cooled to 0 °C, and 0.11 mL (1.3 mmol) of diketene was added dropwise. The reaction was warmed to rt and was stirred for 2 h. After this time the volatiles were removed *in vacuo* and the residue was dissolved in 10 mL of benzene. A 138-mg (1.1 mmol) sample of mesyl azide was added followed by 0.33 mL (2.4 mmol) of Et_3N. The mixture was stirred at rt for 8 h, and the solvent was removed under reduced pressure. Silica gel chromatography of the residue afforded 0.22 g (82%) of *N*-(2-diazo-1,3-oxobutyl)-1-(phenylethynyl)pyrrolidine (**42**) as a viscous yellow oil: IR (neat) 2110, 1705, 1645, 1285, 1230, and 1050 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.93 (m, 1H), 2.12 (m, 2H), 2.29 (m, 1H), 2.36 (s, 3H), 3.54 (m, 2H), 4.86 (dd, 1H, J = 6.7 and 5.1 Hz), 7.23 (m, 3H), and 7.33 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 24.2, 27.8, 33.6, 47.7, 73.9, 83.6, 87.5, 122.3, 128.2, 128.5, 131.7, 159.5, and 190.5.

A 53 mg (0.19 mmol) sample of diazoamide **42** was dissolved in 20 mL of benzene, and 5 mg of rhodium(II) octanoate was added. The mixture was heated at reflux for 30 min. Removal of the solvent under pressure and purification of the residue by silica gel chromatography gave 37 mg (78%) of furan **44** as a yellow oil: IR (neat) 2110, 1705, 1687, 1625, 1430, and 1346 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.04 (m, 4H), 2.53 (s, 3H), 3.30 (m, 1H), 3.71 (ddd, 1H, J = 17.0, 8.5, and 2.9 Hz), 4.74 (dd, 1 H, J = 10.7 and 5.5 Hz), 7.27 (m, 2H), 7.42 (m, 2H), and 7.55 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 12.9, 28.1, 29.6, 42.0, 60.0, 123.1, 123.5, 125.7, 127.1, 128.8, 130.0, 143.0, 147.0, and 166.4; HRMS calcd for $C_{16}H_{15}NO_2$ 253.1103, found 253.1098.

Preparation and Rhodium-Catalyzed Decomposition of *N*-(2-Diazoacetyl)-1-(phenylethynyl)pyrrolidine (43). A 0.18-g (0.63 mmol) sample of *N*-(2-diazo-1,3-oxobutyl)-1-(phenylethynyl)pyrrolidine (**42**) was dissolved in a mixture containing 5 mL of CH_2Cl_2 and 1 mL of pyrrolidine, and the solution was stirred at rt for 3 h. Removal of the solvent under reduced pressure followed by silica gel chromatography gave 0.11 g (75%) of *N*-(2-diazoacetyl)-1-(phenylethynyl)pyrrolidine (**43**): IR (neat) 1608, 1405, and 1335 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.96 (bs, 1H), 2.12 (bs, 3H), 3.30–3.66 (m, 2H), 4.40 (bs, 0.5H), 4.88–5.22 (m, 1.5H), 7.25 (m, 3H), and 7.38 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 23.5, 28.8, 46.7, 48.4, 49.1, 125.6, 128.2, 128.7, 131.9, and 164.4.

A solution containing 46 mg (0.19 mmol) of the above diazoamide and 1 mL (10.5 mmol) of ethyl vinyl ether in 10 mL of benzene was treated with a catalytic amount of rhodium(II) octanoate. The reaction was stirred at rt for 2 h. The solvent and excess ethyl vinyl ether were removed under reduced pressure, and the residue was subjected to silica gel chromatography to give 35 mg (84%) of cyclopropyl ether **45** as a clear oil: IR (neat) 1705, 1632, 1445, and 1340 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.96 (m, 1H), 1.12 (t, 3H, J = 7.0 Hz), 1.33 (m, 2H), 1.46 (bt, 1 H, J = 8.8 Hz), 1.75 (m, 1H), 1.96–2.22 (m, 2H), 3.18 (m, 1H), 3.41 (m, 1H), 3.62 (q, 2H, J = 7.0 Hz), 4.13 (dd, 1H, J = 10.2 and 5.8 Hz), 5.42 (s, 1H), 7.27 (m, 3H), and 7.41 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 14.9, 15.1, 21.2, 23.3, 29.7, 34.4, 46.0, 61.0, 66.5, 128.0, 128.2, 128.3, 128.5, 131.6, 131.8, and 148.6; HRMS calcd for $C_{18}H_{21}NO_2$ (H^+ + 1) 284.1650, found 284.1648.

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Supplementary Material Available: ^{1}H-NMR and ^{13}C-NMR spectra (75 MHz) for new compounds lacking analyses (11 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.