Articles

Rhodium(II)-Catalyzed Cyclization of 2-Alkynyl 2-Diazo-3-oxobutanoates as a Method for Synthesizing Substituted Furans†

Albert Padwa* and Frederick R. Kinder

Department of Chemistry, Emory University, Atlanta, Georgia 30322

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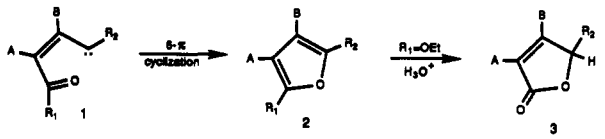
A series of 2-alkynyl 2-diazo-3-oxobutanoates, when treated with a catalytic quantity of rhodium(II) acetate, were found to produce furo[3,4-c]furans in good yield. The reaction proceeds by addition of a rhodium-stabilized carbenoid onto the acetylenic π-bond to give a vinyl carbenoid which subsequently cyclizes onto the neighboring carbonyl group to produce the furan ring. In a similar manner, indeno[1,2-c]furans were produced from 2-butynyl 2-diazoarylacetates. Compounds substituted with methyl groups on the propargylic carbon atom cyclized at a slower rate. This rate diminution is attributed to the fact that the unsubstituted propargyl group can more easily achieve the required conformation for cyclization. C–H insertion was found to compete with furan formation when an alkyl group was attached to the keto functionality of the starting diazo acetoacetate. Diazo alkynyl sulfones undergo a novel oxygen transfer reaction when treated with rhodium(II) acetate at 80 °C. The cyclized product is formed by sulfone oxygen attack onto the vinyl carbenoid producing a dipolar species which subsequently collapses to give the butenolide sulfoxide.

Furans and butenolides are present in many natural products which exhibit interesting biological activity.[1-6] Furans are also useful synthetic intermediates, as they participate in inter- and intramolecular 4 + 2-cycloadditions and can also undergo oxidative conversion to a variety of products.[7-10] New synthetic methods leading to this ring system are therefore of considerable interest. Within the broad domain of cyclization reactions in the field of heterocyclic synthesis, we became particularly interested in the 6π-electrocyclization of alkenone carbenes (i.e., 1 → 2) as a method for synthesizing furans.[11] Transformations of this type are of considerable synthetic utility, since the vast majority of furanosesquiterpenes are functionalized at C-3 (A) and C-4 (B) of the furan ring.[12,13] Use of an ester group (R^1 = OEt) also allows for transformation of 2 to the corresponding butenolide system 3. Formation of five-membered rings by 6π-electrocyclization is a well-precedented process in heterocyclic chemistry.[14-17] Several different synthetic approaches to alkenone carbenes have been developed over the years, producing intermediates that display common trends in their reactivity.[18-23]



1 2 3

Our projected application of this strategy is outlined in Scheme I.[24] The key intermediate in this approach is the acetylenic diazo dicarbonyl compound 4, which should afford the furo[3,4-c]furan ring system 6 in a single step by treatment with a rhodium(II) catalyst. In an ongoing series of papers,[25] our group as well as Hoye's[26] have shown

† Dedicated to my good friend and former colleague Leon Mandell on the occasion of his 65th birthday.

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(25) Padwa, A.; Austin, D. J.; Xu, S. L. *J. Org. Chem.* **1992**, 57, 1330. Padwa, A.; Krumpe, K. E.; Zhi, L. *Tetrahedron Lett.* **1989**, 2623. Padwa, A.; Chiacchio, U.; Gareau, Y.; Kassir, J. M.; Krumpe, K. E.; Schoffstall, A. M. *J. Org. Chem.* **1990**, *55*, 414. Padwa, A.; Krumpe, K. E.; Gareau, Y.; Chiacchio, U. *J. Org. Chem.* **1991**, *56*, 2523. Padwa, A.; Austin, D. J.; Xu, S. L. *Tetrahedron Lett.* **1991**, 4103.
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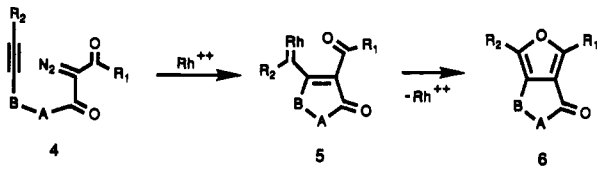
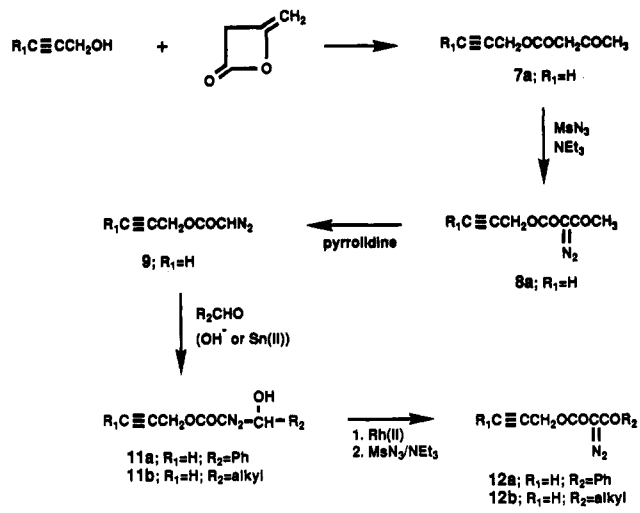
0022-3263/93/1958-0021$04.00/0

Scheme I



Scheme II

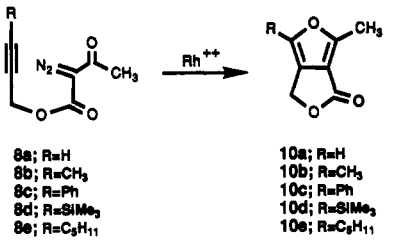


that the rhodium(II)-catalyzed reaction of α-diazo ketones related to **4** results in cyclization of the initially formed metal carbenoid onto the tethered alkyne unit to give an intermediate (**5**), in which carbenelike reactivity has been transferred to one of the original alkyne carbon atoms. The potential for many diverse chemical pathways exists through the further chemistry of the reactive metallocarbenoid. In this paper we describe the scope of the Rh(II)-catalyzed cyclization of a series of 2-alkynyl 2-diazo-3-oxobutanoates and document its application as a means of synthesizing a variety of furo[3,4-*c*]furans of type **6**.

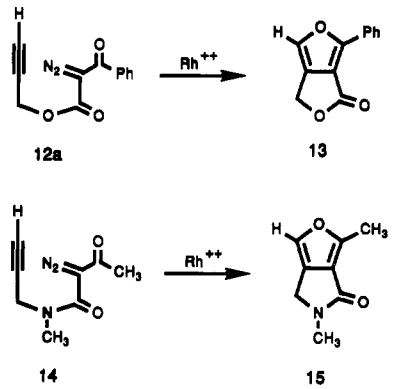
Results and Discussion

The preparation of the propargyl diazo ketoacetate system was straightforward and high yielding (Scheme II). An appropriately substituted propargyl alcohol was acylated with diketene to give the alkynyl 3-oxobutanoate derivative **7**. Diazo transfer to the activated methylene position was accomplished using mesyl azide and stoichiometric triethylamine.[27] Diazo keto ester **8a** could easily be deacylated by simply stirring with pyrrolidine. Condensation of the resulting diazo ester **9** with benzaldehyde in methanolic potassium hydroxide solution as reported by Wenkert[28] afforded the 2-diazo hydroxy ester **11a**. Treatment of this compound with a catalytic amount of rhodium(II) acetate gave the benzoyl substituted keto ester (R_2 = Ph) which was subsequently converted with mesyl azide to **12a** (R_1 = H; R_2 = Ph) in 52% overall yield for **9**.[29] Alkyl-substituted diazo keto esters (i.e., **12b**; R_2 = alkyl) were most conveniently prepared from the reaction of diazo ester **9** and an aliphatic aldehyde in the presence of tin(II) chloride.[29,30] Diazo hydroxy ester **11b** was formed as a transient species which further rearranged in the presence of the tin catalyst[29,30] to give an intermediate β-keto ester which was subsequently transformed into the desired aliphatic diazo keto ester **12b** using mesyl azide. Our results indicate that diazo esters condense best with aromatic aldehydes using the base-catalyzed conditions whereas aliphatic aldehydes react best under the Lewis acid-catalyzed reaction conditions. It should be noted that although β-keto esters can be prepared by a variety of methods,[31] only a few of them show high regioselectivity when applied to unsymmetrical systems,[32-37] as is the case above.

The alkynyl 2-diazo-3-oxobutanoates **8a–8e** were all efficiently converted to the expected furo[3,4-*c*]furans in high yield (>70%) by treatment with a catalytic amount of rhodium(II) acetate at 80 °C. The reaction was quite



versatile with regard to the nature and number of substituents incorporated into the furo[3,4-*c*]furan ring. An analogous cyclization occurred with diazo keto ester **12a** affording furan **13** in 76% isolated yield. When the reaction was carried out with the closely related amide **14**, there was no notable difference in yield or reaction time required for completion.



Likewise, indeno[1,2-*c*]furans **18a–c** were produced in 45–60% yield from the diazo precursors **16a–c**. Here the vinyl carbenoid **17** undergoes aromatic C–H insertion. The

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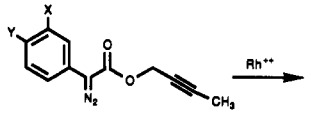
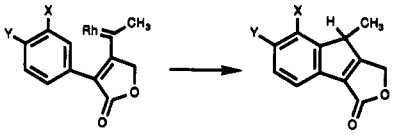
diazo precursors **16b** and **16c** were prepared in order to evaluate the effect of an electron-withdrawing group on the C–H insertion process. Interestingly, there seemed to be little effect displayed by the substituent group, and indeno[1,2-*c*]furans **18b** and **18c** were isolated as the exclusive products. The fact that the insertion occurs ortho to the nitro group (i.e., **16c** → **18c**) rather than producing a mixture of ortho and para isomers suggests that subtle factors play a role in this process.[38]



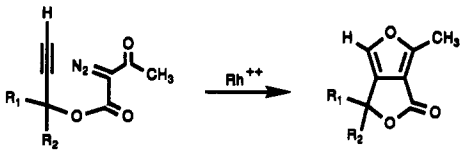
16a; X=Y=H
16b; X=H, Y=NO_2
16c; X=NO_2; Y=H



17

18a; X=Y=H
18b; X=H, Y=NO_2
18c; X=NO_2; Y=H

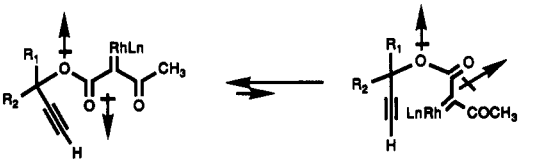
It has long been recognized that the cyclization of acyclic precursors is significantly accelerated by alkyl substituents.[39-42] Certain aspects of this general phenomena, which has been popularized as the *gem dialkyl effect*, have been explained on a purely thermodynamic basis.[43] Other aspects have been related specifically to the *Thorpe–Ingold effect*[40] and to the release of steric strain in the ground state upon ring closure[44] and also to the decrease in unprofitable rotamer distribution in the ground state upon alkyl substitution.[45-49] The latter explanation is a qualitative version of the classical Winstein–Holness equation.[50] More recent results by Jung and Gervay showed that the rate acceleration is due primarily to the reactive conformer effect and not to angle compression.[51] Over the years numerous quantitative studies related to the *gem-dialkyl promoting effect* have been reported.[51] Consequently, one might expect to encounter a similar rate acceleration in cyclization as the degree of substitution is increased about the α-position of the alkynyl 2-diazo-3-oxobutanoate system. Most surprisingly, *we found the exact opposite*. Thus, the *gem*-dimethyl propargyl ester **20** (R_1 = H; R_2 = Me) produced the furo[3,4-*c*]furan ring at a slower rate (ca. 50%) than the monomethyl propargyl ester **19** (R_1 = H; R_2 = Me), which in turn cyclized at a slower rate (ca. 50%) than the unsubstituted ester **8a**.[52]



8a; R_1=R_2=H
19; R_1=CH_3; R_2=H
20; R_1=R_2=CH_3

10a; R_1=R_2=H
21; R_1=CH_3; R_2=H
22; R_1=R_2=CH_3

At first glance, these results would seem to contradict the Thorpe–Ingold effect which would predict an exactly opposite trend in rates. The rhodium carbenoid derived from the diazo keto ester exists primarily in the *Z* or s-trans conformation about the ester bond (i.e., **23**), since it is



23Z (s-trans) 24E (s-cis)

well-known that ester are more stable in this conformation for several reasons, one of which is to minimize overall dipole effects.[53] In this orientation, intramolecular cyclization of the rhodium carbenoid on the alkyne π-bond cannot occur. In order to cyclize, there must be a rotation about this ester bond to give the *E* or s-cis conformer **24**, which can then achieve the necessary transition state for cyclization. We believe that a lower population of the reactive conformer exists with the bulkier propargyl group and consequently a retardation in rate of cyclization occurs. Thus, our rationale to account for the observed cyclization rates is that the unsubstituted propargyl group can more easily attain the required transition state for cyclization as compared to the methyl-substituted substrate and therefore cyclizes more rapidly.[54] We have used the Still–Steliou Model 2.94 program to model energy differences between the two conformations of the diazo keto esters. Global minima were found by making use of multicomformer generation of Model (TTY, Conf, Statistical, Coordinate) followed by Batch minimization using Bakmdl. The calculations clearly show a greater energy difference for the conversion of the s-trans to s-cis ester conformations for the *gem*-dimethyl case than for the monomethyl and unsubstituted cases (see Table I).[56]

Further examples which support the generality of the 1,5-cyclization reaction were sought. With this in mind,

(38) For an earlier report describing a dramatic substituent effect (NO_2 group) on the C–H insertion process, see: Etkin, N.; Babu, S. D.; Fooks, C. J.; Durst, T. *J. Org. Chem.* **1990**, *55*, 1093.
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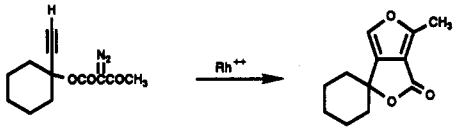
(52) Relative rates of cyclization were derermined by carrying out the reaction in sealed NMR tubes and following the appearance of the furo[3,4-*c*]furan ring system.
(53) Dale, J. *Stereochemistry and Conformational Analysis*; Verlag Chemie: New York, 1978; pp 83–85. Testa, B. *Principles of Organic Stereochemistry*; Marcel Dekker: New York, 1979; p 105. Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis*; Interscience: New York, 1965; p 21.
(54) This rationale is based on the assumption that the rate-limiting step involves cyclization of the rhodium carbenoid rather than nitrogen extrusion. The rhodium carbenoid derived from the 2-diazo-3-oxobutanoate system would have to be suffiently long lived to be influenced by the substituent groups on the propargylic side chain. It is also conceivable that under the experimental conditions used (i.e., sealed tube thermolysis), the rhodium carbenoid reacts with nitrogen to regenerate the diazo ketoester.[55]
(55) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H. P. *J. Am. Chem. Soc.* **1985**, *107*, 7597.
(56) The difference in energy between the *Z* and *E* conformers for methyl formate (4.8 kcal/mol) and for methyl acetate (8.5 kcal/mol) has been reported by: Blom, C. E.; Gunthard, H. H. *Chem. Phys. Lett.* **1981**, *84*, 267.

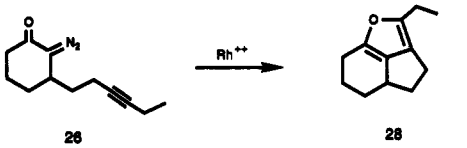
Table I. Calculated Energy Differences between s-Trans and s-Cis Conformations

R_1	R_2	E(s-trans)	E(s-cis)	ΔE (kcal)
H	H	6.85	10.94	4.09
CH_3	H	7.55	11.76	4.21
CH_3	CH_3	8.80	15.30	6.50

we investigated the rhodium(II)-catalyzed reactions of diazo ester **25** and diazo ketone **26**. In both cases the initially formed vinylcarbenoid cyclized cleanly to give furans **27** and **28** in 75% and 72% yield, respectively.[25] As a direct analogy for the cyclization step, there are prior conversions of α-carbene α,β-unsaturated carbonyl compounds to furans,[57] as well as formally related cyclizations of both all-carbon carbenes and also related species containing other heteroatoms.[58]



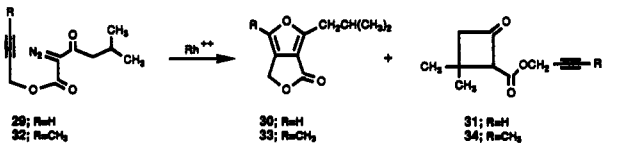
25 27



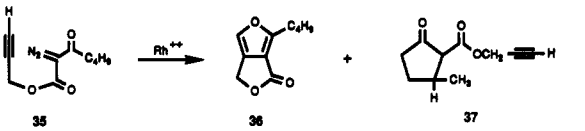
26 28

Of particular importance in catalytic synthesis employing diazocarbonyl intermediates are intramolecular processes involving C–H insertions.[59-61] It is well-documented that cyclization of the electrophilic rhodium–carbene complex leads to preferential formation of five-membered rings in acyclic, conformationally mobile systems[62] in which the order of ractivity of the C–H site is methine > methylene ≫ methyl.[63] There have also been several recent examples of C–H insertions leading to four- and six-membered rings as well as facile C–H bond insertion in both a constrained rigid[64] and even acyclic systems.[65] These results indicate that site selectivity depends on the nature of the α-diazo carbonyl compound and also suggests that it is governed by steric and conformational factors as well as electronic factors. During the course of our studies dealing with the 1,5-electrocyclization reaction of alkynyl

Scheme III

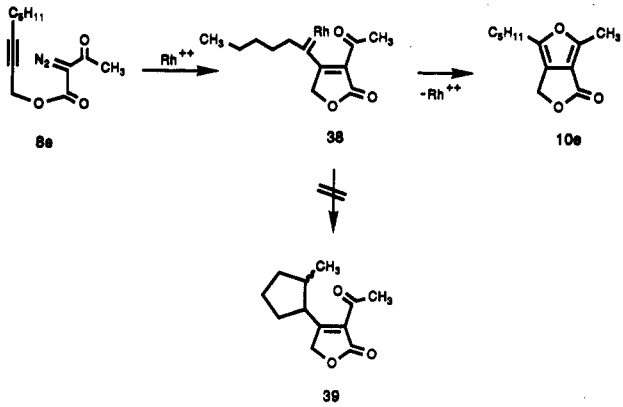


29; R=H 30; R=H 31; R=H
32; R=CH_3 33; R=CH_3 34; R=CH_3



35 36 37

2-diazo-3-oxobutanoates, we found that the C–H insertion reaction can compete with furan formation when an alkyl group was attached to the keto functionality. Thus, a 1:1 mixture of cyclization (**30**) and insertion (**31**) products was observed when diazo ester **29** was treated with rhodium(II) acetate in benzene at 80 °C (Scheme III). The ratio could be slightly altered to favor cyclobutanone formation (i.e., **33**:**34** = 1:1.5) when a methyl group was placed onto the terminal alkyne. In both of these cases, insertion into the tertiary C–H bond to give a cyclobutanone is favored over insertion into one of the methyl groups. However, the unbranched diazo ester **35** favored the five ring insertion pathway over cyclization (**36**:**37** = 1:3). Since carbocycle formation via C-H insertion shows a strong preference for five-membered rings,[64] we also studied the rhodium(II) catalyzed behavior of diazoacetoacetate **8e**. In principle, the resulting vinyl carbenoid **38** could either cyclize or insert into the side chain. However, the only product that could be detected (85% yield) corresponded to furan **10e**. The highly electrophilic carbenoid intermediates **38** is easily intercepted by the adjacent carbonyl group which is in close proximity to the carbenoid center. The C–H insertion pathway possesses a much larger negative entropy of activation, and this would account for why none of **39** is observed from diazoacetoacetate **8e**.



8e 38 10e

39

α-Diazo sulfones have previously been used for carbene-mediated C–H insertion and cyclopropanation reactions.[66-68] In order to appraise the role of this substituent group on the cyclization process, we prepared diazo alkynyl sulfones **40** and **41**. Treatment of these compounds with

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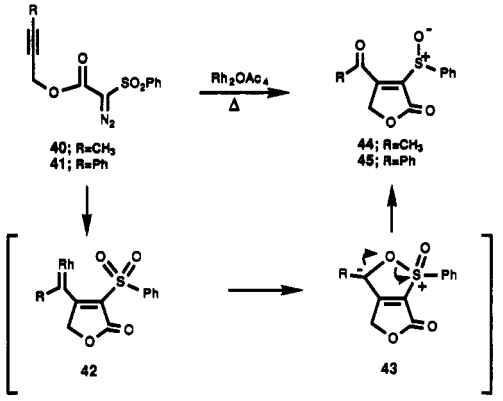
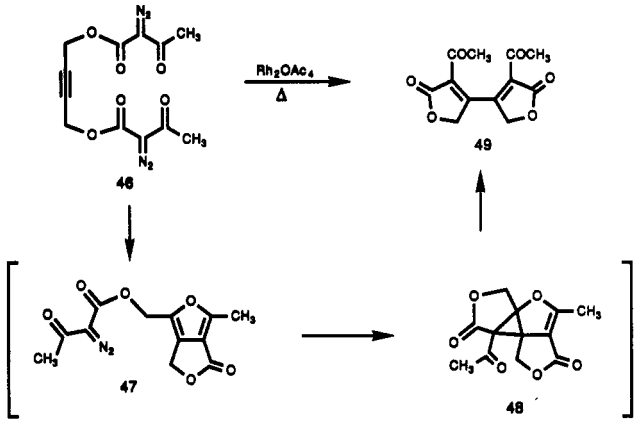
Rh(II) acetate at 80 °C gave sulfoxides **44** and **45** in 60 and 90% yield, respectively. This novel oxygen-transfer reaction can be rationalized by sulfone oxygen attack onto the vinyl carbenoid **42** producing the dipolar species **43**. Subsequent collapse of this transient affords the ring-opened butenolides **44** and **45**.[69]



Very few examples of the chemistry of bis(diazo ketones) have been reported.[70] This is not surprising when one considers the number of possible complications that may arise from the combination of two reactive carbenoid centers in the same molecule. However, should the rhodium(II)-catalyzed carbenoid formation occur in a stepwise fashion, then a single product might result from such a process. With this in mind, the symmetrical bis(diazo ester) **46** was prepared in the normal manner. Heating a benzene solution of **46** with Rh_2OAc_4 at reflux gave rise to a 90% yield of bis(butenolide) **49**. The



mechanism of this reaction requires that one diazo ester group react with the alkyne to generate a vinyl carbenoid which subsequently cyclizes to produce furan **47**. Further reaction of **47** with rhodium acetate generates a second carbenoid which undergoes an intramolecular cyclopropanation onto the furan ring.[71] The resulting cycloadduct **48** then undergoes a typical cyclopropanated furan fragmentation reaction to give the symmetrical product **49**.[72]

In conclusion, the facility with which the rhodium(II)-catalyzed cyclization reaction of 2-alkynyl 2-diazo-3-oxobutanoates occurs makes these molecules particularly attractive for the synthesis of a wide variety of furo[3,4-*c*]furans. The nature of the substituents that flank the diazomethylene group not only controls the formation of the vinyl carbenoid but also the products that result from the interaction of that substituent with the adjacent reactive center. We are continuing to explore the scope and mechanistic details of these electrocyclization reactions and will report additional findings at a later date.

Experimental Section

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

General Procedure for the Preparation and Rhodium(II) Acetate Catalyzed Cyclization of 2-Alkynyl 2-Diazo-3-oxobutanoates. A solution containing 34 mmol of the appropriate propargylic alcohol, 37 mmol of diketene, and 0.1 mL of triethylamine in 100 mL of THF was stirred at 25 °C for 16 h. To this solution was added 5.0 g (41 mmol) of mesyl azide followed by 9.6 mL (69 mmol) of triethylamine. The solution was stirred for 16 h at 25 °C. Concentration of the mixture under reduced pressure followed by silica gel chromatography gave the appropriate diazo 3-oxobutanoate. To a stirred solution containing 12.0 mmol of the diazo compound in 200 mL of dry benzene was added 30 mg of rhodium(II) acetate. The mixture was heated at reflux for 3 h. At the end of this time the solution was concentrated under reduced pressure and the dark yellow residue was purified by chromatography. This method was used to prepare the following compounds:

2-Propynyl 2-diazo-3-oxobutanoate (8a) was prepared in 79% yield from propargyl alcohol: IR (neat) 2140, 1740, 1640, 1450, and 1370 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.45 (s, 3 H), 2.50 (t, 1 H, J = 2.0 Hz), and 4.85 (d, 2 H, J = 2.0 Hz). This diazo compound was converted into 1-oxo-6-methyl-1*H*,3*H*-furo[3,4-*c*]furan (**10a**) (75%): mp 98–99 °C; IR ($CHCl_3$) 1770, 1650, 1590, 1395, 1350, and 1180 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.41 (s, 3 H), 5.05 (d, 2 H, J = 1.0 Hz), and 7.10 (t, 1 H, J = 1.0 Hz). Anal. Calcd for $C_7H_6O_3$: C, 60.87; H, 4.38. Found: C, 60.80; H, 4.43.

2-Butynyl 2-diazo-3-oxobutanoate (8b) was prepared from 2-butyn-1-ol in 72% yield: IR (neat) 2150, 1725, 1655, 1310, 1060, 965, and 740 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.83 (t, 3 H, J = 2.1 Hz), 2.44 (s, 3 H), and 4.76 (q, 2 H, J = 2.1 Hz). This diazo compound was converted into 1-oxo-4,6-dimethyl-1*H*,3*H*-furo[3,4-*c*]furan (**10b**) (75%): mp 74–75 °C; IR (KBr) 1770, 1630, 1380, 1270, 1185, 1035, and 975 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 2.19 (s, 3 H), 2.38 (s, 3 H), and 5.00 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 12.2, 12.3, 64.0, 114.2, 124.4, 139.5, 149.4, and 165.5; m/z 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.

3-Phenyl-2-propynyl 2-diazo-3-oxobutanoate (8c) was prepared from 3-phenyl-2-propyn-1-ol in 59% yield: IR (neat) 2150, 1730, 1660, 1440, 1370, and 1320 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.45 (s, 3 H), 5.10 (s, 2 H), and 7.31 (m, 5 H). This diazo compound was converted into 1-oxo-4-phenyl-6-methyl-1*H*,3*H*-furo[3,4-*c*]furan (**10c**) (82%): mp 115–116 °C; IR ($CHCl_3$) 1770, 1650, 1620, 1500, 1450, and 1355 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.50 (s, 3 H), 5.33 (s, 2 H), and 7.35 (s, 5 H). Anal. Calcd for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71. Found: C, 72.73; H, 4.70.

3-(Trimethylsilyl)-2-propynyl 2-diazo-3-oxobutanoate (8d) was prepared from 3-(trimethylsilyl)-2-propyn-1-ol in 70% yield: IR (neat) 2140, 1730, 1650, 1440, 1370, 1210, and 1150 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.25 (s, 9 H), 2.53 (s, 3 H), and 4.85 (s, 2 H). This diazo compound was converted into 1-oxo-4-(trimethylsilyl)-6-methyl-1*H*,3*H*-furo[3,4-*c*]furan (**10d**) (93%): mp 100–101 °C; IR (neat) 1793, 1439, 1373, and 1028 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.10 (s, 9 H), 2.20 (s, 3 H), and 4.91 (s, 2 H). Anal. Calcd for $C_{10}H_{14}N_2Si$: C, 57.11; H, 6.71. Found: C, 57.19; H, 6.74.

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2-Octynyl 2-diazo-3-oxobutanonate (8e) was prepared from 2-octyn-2-ol[73] in 85% yield: IR (neat) 2140, 1725, 1710, 1660, 1430, 1315, and 1260 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.92 (m, 3 H), 1.43 (m, 6 H), 2.20 (m, 2 H), 2.45 (s, 3 H), and 4.85 (t, 2 H, J = 2 Hz). This diazo compound was converted into 1-oxo-4-pentyl-6-methyl-1*H*,3*H*-furo[3,4-*c*]furan (**10e**) in 85% yield: IR (neat) 1770, 1665, 1625, 1465, 1350, 1270, and 1185 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.92 (t, 3 H, J = 6 Hz), 1.54 (m, 6 H), 2.55 (s, 3 H), 2.62 (t, 2 H, J = 6 Hz), and 5.10 (s, 2 H). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.75. Found: C, 69.31, H, 7.74.

2-Propynyl 2-Diazo-3-oxo-3-phenylpropionate (12a). A solution containing 8.3 mL (140 mmol) of propargyl alcohol, 10 mL (130 mmol) of diketene, and 1 mL of triethylamine in 200 mL of dry THF was stirred at 25 °C for 12 h. To this solution was added 19 g (156 mmol) of mesyl azide and 27 mL (195 mmol) of triethylamine. The reaction mixture was stirred at 25 °C for 16 h. To this solution was added 22 mL (264 mmol) of pyrrolidine, and the mixture was stirred at 25 °C for an additional 3 h. The solution was concentrated under reduced pressure, and the residue was purified by silica gel chromatography to give 15.7 g (98%) of 2-propynyl diazoacetate (**8a**): IR (neat) 2125, 1695, 1440, 1390, 1360, and 1240 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.61 (t, 1 H, J = 2 Hz), 4.85 (d, 2 H, J = 2 Hz), and 4.91 (s, 1 H).

To a solution containing 3.0 g (24 mmol) of **8a** and 2.5 mL (24 mmol) of benzaldehyde in 5 mL of ethanol at 25 °C was slowly added 1 mL of a 10% KOH–ethanol solution. The solution was stirred for 1 h and was extracted with CH_2Cl_2. The organic layer was dried over sodium sulfate and concentrated under reduced pressure to a volume of ca. 100 mL. To this solution was added 30 mg of rhodium(II) acetate, and the reaction mixture was stirred for 3 h at 25 °C. The resulting solution was concentrated under reduced pressure to give a red oil which was dissolved in 150 mL of THF. To this solution was added 7 mL (50 mmol) of dry triethylamine and 2.9 g (24 mmol) of mesyl azide. The reaction mixture was stirred at 25 °C for 12 h. Concentration of the dark red solution under reduced pressure afforded an oil that was purified by silica gel chromatography to give 2.86 g (52%) of 2-propynyl 2-diazo-3-oxo-3-phenylpropionate (**12a**): IR (neat) 2160, 1740, 1640, 1370, and 1180 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.61 (t, 1 H, J = 2 Hz), 4.85 (d, 2 H, J = 2 Hz), and 7.55 (m, 5 H). This diazo compound was converted into 1-oxo-6-phenyl-1*H*,3*H*-furo[3,4-*c*]furan (**13**) (76%): mp 120–121 °C; IR ($CHCl_3$) 1760, 1630, 1570, 1500, and 1365 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 5.25 (d, 2 H, J = 1.0 Hz), 7.30 (t, 1 H, J = 1.0 Hz), 7.45 (m, 3 H), and 8.15 (m, 2 H). Anal. Calcd for $C_{12}H_8O_3$: C, 72.00; H, 4.03. Found: C, 71.91; H, 4.05.

***N*-Methyl-*N*-(2-propynyl)-2-diazo-3-oxobutanamide (14)** was prepared from *N*-methylpropargylamine in 63% yield; IR (neat) 2120, 1750, 1640, 1480, 1390, and 1280 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.45 (m, 4 H), 3.15 (s, 3 H), and 4.25 (d, 2 H, J = 2 Hz). This material was converted into 3,5-dimethyl-4-oxo-4*H*,6*H*-furo[3,4-*c*]pyrrole (**15**) (74%): mp 61–62 °C; IR ($CHCl_3$) 1710, 1590, 1480, 1425, and 1390 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.45 (s, 3 H), 3.05 (s, 3 H), 4.20 (d, 2 H, J = 1 Hz), and 7.10 (t, 1 H, J = 1 Hz). Anal. Calcd for $C_8H_9NO_2$: 63.56; H, 6.00; N, 9.27. Found: C, 63.45; H, 5.94; N, 9.25.

Rhodium(II) Octanoate Catalyzed Cyclization of 2-Butynyl 2-Diazophenylacetate (16a). To a 7.0-g (100 mmol) sample of 2-butyn-1-ol at 0 °C was added dropwise 15.45 g (100 mmol) of phenylacetyl chloride with stirring over a period of 20 min. The solution was warmed to 25 °C and was then heated for 15 min at 100 °C. The mixture was distilled to give 16.5 g (88%) of 2-butynyl phenylacetate: bp 170–175 °C (10 mm); IR (neat) 1745, 1500, 1460, 1245, 1150, 990, and 710 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.82 (t, 3 H, J = 3.0 Hz), 3.68 (s, 2 H), 4.67 (q, 2 H, J = 3.0 Hz), and 7.34 (m, 5 H).

To 7.04 g (80 mmol) of acetic–formic anhydride[74] in 25 mL of CCl_4 was added dropwise with stirring 5.6 g of 2-butyn-1-ol over a 15-min period. Stirring was continued for 24 h, and then the solution was washed with a saturated sodium bicarbonate solution, dried over magnesium sulfate, and concentrated under reduced pressure. The residual oil was distilled to give 10.2 g of 2-butynyl 1-formate, bp 130–145 °C. To 25 mL of ether in a flame-dried flask under a nitrogen atmosphere was added 720 mg of NaH mineral oil dispersion. After the solution was stirred for 10 min, 0.94 g (5.0 mmol) of 2-butynyl phenylacetate and 3.0 g (30 mmol) of 2-butynyl 1-formate was added dropwise with stirring at 0 °C and the mixture was allowed to stir overnight at 25 °C. To the reddish-brown mixture was added 1.82 g of mesyl azide in 25 mL of ether, and the mixture was stirred for 2 h at 25 °C. The solution was concentrated under reduced pressure, and 100 mL of CH_2Cl_2 was added to the residue. The organic layer was washed with 50 mL of a 10% NaOH solution. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layer was dried and concentrated under reduced pressure. The resulting residue was purifed by chromatography to give 600 mg (56%) of 2-butynyl 2-diazophenylacetate (**16a**): IR ($CHCl_3$) 2125, 1725, 1520, 1370, 1175, and 775 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.85 (t, 3 H, J = 3.0 Hz), 4.87 (q, 2 H, J = 3.0 Hz), and 7.30 (m, 5 H).

To an 80-mg (0.37 mmol) sample of **16a** dissolved in 15 mL of benzene was added 3 mg of rhodium(II) octanoate in a flask fitted with a capillary bubbler. Evolution of nitrogen was complete after 4 h at 25 °C, and stirring was continued overnight. The mixture was washed with a 10% sodium bicarbonate solution, dried over magnesium sulfate, concentrated under reduced pressure, and purified by silica gel chromatography to give 35 mg of 3-oxo-8-methyl-1*H*,3*H*-indeno[1,2-*c*]furan (**18a**) as a pale yellow oil in 50% yield: IR (neat) 1760, 1605, 1460, 1310, 1020, 990, and 780 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.46 (d, 3 H, J = 7.8 Hz), 3.81 (q, 1 H, J = 7.8 Hz), 5.12 (s, 2 H), 7.32 (m, 2 H), 7.44 (m, 1 H), and 7.67 (m, 1 H); ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 14.8, 41.1, 68.4, 120.3, 123.1, 126.0, 126.7, 126.8, 128.2, 128.7, 151.6, and 176.7; *m/e* 186 (M^+), 172, 157, 142, 129 (base), and 115. Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.24; H, 5.38.

Rhodium(II) Acetate Catalyzed Cyclization of 2-Butynyl 2-Diazo-2-(4-nitrophenyl)acetates. To a stirred solution containing 3.0 g (16 mmol) of 4-nitrophenylacetic acid and 100 mL of THF at 25 °C was added 4.0 g (25 mmol) of carbonyldiimidazole. The reaction mixture was stirred for 18 h at 25 °C, and then 1.9 mL (25 mmol) of 2-butynol was added in one portion. The solution was stirred for 10 h, and then 2.4 g (20 mmol) of mesyl azide and 4.6 mL (33 mmol) of triethylamine were each added in one portion. The reaction mixture was stirred for 16 h and concentrated under reduced pressure. The resultant residue was purified by chromatography to give 3.5 g (81%) of 2-butynyl 2-diazo-2-(4-nitrophenyl)acetate (**16b**): mp 116–117 °C; IR ($CHCl_3$) 2090, 1695, 1590, 1505, 1340, 1250, and 1160 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.81 (t, 3 H, J = 2 Hz), 4.85 (q, 2 H, J = 2 Hz), 7.60 (dd, 2 H, J = 9 and 1 Hz), and 8.25 (dd, 2 H, J = 9 and 1 Hz).

To a stirred solution containing 200 mg (0.77 mmol) of **16b** and 10 mL of benzene was added 10 mg of rhodium(II) acetate. The solution was heated at reflux for 2 h, and the mixture was concentrated under reduced pressure. The residue was purified to give 100 mg (56%) of 3-oxo-6-nitro-8-methyl-1*H*,3*H*-indeno[1,2-*c*]furan (**18b**): mp 180–181 °C; IR ($CHCl_3$) 1760, 1620, 1510, 1340, and 1120 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.55 (d, 3 H, J = 7 Hz), 3.95 (d, 1 H, J = 7 Hz), 5.23 (s, 2 H), 7.75 (d, 1 H, J = 9 Hz), 8.20 (d, 1 H, J = 9 Hz), and 8.25 (s, 1 H). Anal. Calcd for $C_{12}H_9NO_4$: C, 62.34, H, 3.92; N, 6.06. Found: C, 62.12; H, 3.85; N, 5.89.

3-Oxo-7-nitro-8-methyl-1*H*,3*H*-indeno[1,2-*c*]furan (16c). 2-Butynyl 2-diazo-2-(3-nitrophenyl)acetate (**16c**) was prepared in a manner similar to that described above starting from 3-nitrophenylacetic acid in 63% yield: mp 105–106 °C; IR ($CHCl_3$) 2100, 1700, 1610, 1345, 1230, and 1150 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.85 (t, 3 H, J = 2 Hz), 4.85 (q, 2 H, J = 2 Hz), 7.50 (m, 1 H), 7.92 (m, 2 H), and 8.35 (m, 1 H). This diazo compound was converted into 3-oxo-7-nitro-8-methyl-1*H*,3*H*-indeno[1,2-*c*]furan (**18c**) in 45% yield: mp 178–179 °C; IR ($CHCl_3$) 1750, 1430, 1360, 1340, and 1130 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.45 (d, 3 H, J = 6 Hz), 4.65 (q, 1 H, J = 6 Hz), 5.25 (s, 2 H), 7.60 (t, 1 H, J = 8 Hz), 8.02 (d, 1 H, J = 8 Hz), and 8.10 (d, 1 H, J = 8 Hz). Anal. Calcd for $C_{12}H_9NO_4$: C, 62.34; H, 3.92. Found: C, 62.63; H, 3.97.

3-Butyn-2-yl 2-diazo-3-oxobutanoate (19) was prepared from 3-butyn-2-ol in 79% yield: IR (neat) 2160, 1720, 1650, 1350, and 1300 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.55 (d, 3 H, J = 7.0 Hz), 2.45 (s, 3 H), 2.60 (d, 1 H, J = 2.0 Hz), and 5.55 (qd, 1 H, J =

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7.0 and 2.0 Hz). This diazo compound was converted into 1-oxo-3,6-dimethyl-1*H*,3*H*-furo[3,4-*c*]furan (**21**) (74%): IR (neat) 1760, 1640, 1585, 1440, 1370, 1320, and 1180 cm^{-1}; NMR ($CDCl_3$) δ 1.55 (d, 3 H, J = 6 Hz), 2.53 (s, 3 H), 5.55 (qd, 1 H, J = 6.0 and 1.0 Hz), and 7.15 (d, 1 H, J = 1.0 Hz). Anal. Calcd for $C_8H_8O_3$: C, 63.15; H, 5.30. Found: C, 63.02; H, 5.32.

2-Methyl-3-butyn-2-yl 2-diazo-3-oxobutanoate (20) was prepared from 2-methyl-3-butyn-2-ol in 58% yield: IR (neat) 2150, 725, 1660, 1370, 1325, and 1250 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.75 (s, 6 H), 2.50 (s, 3 H), and 2.65 (s, 1 H). This diazo compound was converted into 1-oxo-3,3,6-trimethyl-1*H*,3*H*-furo[3,4-*c*]furan (**22**) (72%): mp 42–43 °C; IR (neat) 1750, 1645, 1590, 1460, 1445, 1390, and 1370 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.65 (s, 6 H), 2.50 (s, 3 H), and 7.15 (s, 1 H). Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 65.14; H, 6.09.

1-Ethynylcyclohex-1-yl 2-diazo-3-oxobutyrate (25) was prepared from 1-ethynylcyclohexanol in 82% yield: mp 75–76 °C; IR (neat) 2160, 1725, 1660, 1450, and 1325 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.60 (m, 6 H), 2.11 (m, 4 H), 2.45 (s, 3 H), and 2.70 (s, 1 H). This diazo compound was converted into 1-oxo-3-spirocyclohexyl-6-methyl-1*H*,3*H*-furo[3,4-*c*]furan (**27**) (75%): IR (neat) 1760, 1640, 1580, 1445, 1320, 1260, and 1180 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.65 (m, 10 H), 2.50 (s, 3 H), and 7.25 (s, 1 H). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.95; H, 6.90.

Preparation and Rhodium(II)-Catalyzed Reaction of 2-Diazo-3-(3-pentynyl)cyclohexanone (26). To 150 mg of magnesium turnings in 5 mL of THF was slowly added 1.0 g (6.2 mmol) of 1-bromo-3-hexyne in 10 mL of THF under a nitrogen atmosphere. After the mixture was stirred for 1 h, a solution containing 150 mg (1.56 mmol) of cyclohexenone and 25 mg of tri-*n*-butylphosphine–copper(I) iodide complex in 15 mL of ether was added dropwise at 0 °C. After the resulting solution for 30 min, 1.11 g (15 mmol) of ethyl formate was added and the mixture was stirred for an additional 10 min at 0 °C. The solution was then poured into a 10% NH_4Cl solution and extracted with ether. The organic layer was washed with a 10% NaOH solution, and the alkaline layer was acidified with an ice-cold 50% HCl solution which was then extracted with ether. The solvent was dried over magnesium sulfate and removed under reduced pressure to leave behind 150 mg (47%) of 2-hydroxymethylene-3-(3-pentynyl)cyclohexanone as a pale yellow oil which was used in the next step without further purification: IR (neat) 1720, 1640, 1470, 1380, and 1325 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.10 (t, 3 H, J = 7.0 Hz), 1.65 (m, 5 H), 2.10–2.50 (m, 7 H), 2.70 (m, 1 H), 8.80 (s, 1 H) and 14.65 (s, 1 H).

To an ice-cold solution containing 0.35 g (1.7 mmol) of the above compound and 0.73 mL of triethylamine in 4 mL of CH_2Cl_2 was added 0.3 g (2.5 mmol) of mesyl azide in 2 mL of CH_2Cl_2. The solution was stirred for 3 h as the temperature was allowed to rise to 25 °C, and then 10 mL of a 1.0 N KOH solution was added and the mixture was stirred at 25 °C for 30 min. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with a dilute KOH solution, followed by water. The solvent was dried over magnesium sulfate and removed under reduced pressure. The resulting residue was purified by silica gel chromatography to give 0.25 g (70%) of 2-diazo-3-(3-pentynyl)cyclohexanone (**26**) as a bright yellow oil: IR (neat) 2080, 1630, 1450, and 1325 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.10 (t, 3 H, J = 7.2 Hz), 1.40 (m, 1 H), 1.61–1.94 (m, 5 H), 2.14 (q, 2 H, J = 7.2 Hz), 2.25–2.35 (m, 4 H) and 3.05 (m, 1 H).

A mixture containing 94 mg (0.46 mmol) of the above diazo ketone and 10 mg of rhodium(II) mandelate in 4 mL of benzene was heated at reflux for 3 h. After removal of the solvent under reduced pressure the crude oil was purified by silica gel chromatography to give 51 mg (72%) of 2-ethyl-2a,7a-furo-3,4,4a,5,6,7-hexahydroindene (**28**) as a clear oil: IR (neat) 1700, 1615, 1460, 1355, 1235, 880, and 860 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 0.73 (dq, 1 H, J = 11.7 and 1.8 Hz), 1.20 (t, 3 H, J = 7.5 Hz), 1.65–1.85 (m, 2 H), 2.03 (m, 2 H), 2.30–2.70 (m, 6 H) and 2.59 (q, 2 H, J = 7.5 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 11.6, 20.8, 23.5, 25.1, 25.7, 30.5, 33.6, 41.6, 123.5, 137.6, 144.3 and 148.3; HRMS calcd for $C_{12}H_{16}O$ 176.1201, found 176.1200.

2-Propynyl 2-Diazo-3-oxo-5-methylhexanonate (29). To a stirred suspension containing 150 mg of tin(II) chloride in 20 mL of CH_2Cl_2 was added 2.0 g (16 mmol) of 2-propynyl diazoacetate **9**. Approximately 10 drops of a 2.0-mL (18 mmol) aliquot of isovaleraldehyde was added to the mixture, and gas evolution was observed within 5 min. The remaining isovaleraldehyde was added dropwise, and the mixture was stirred for 1.5 h at 25 °C. The solution was suction-filtered through a pad of silica gel using a fritted glass funnel and washed with excess CH_2Cl_2. The filtrate was concentrated under reduced pressure and then redissolved in 25 mL of THF. To this solution was added 2.0 g (16 mmol) of mesyl azide and 4.0 mL (28 mmol) of triethylamine, and the mixture was stirred for 16 h at 25 °C. Concentration of the solution under reduced pressure afforded a yellow oil that was purified by silica gel chromatography to give 2.8 g (83%) of 2-propynyl 2-diazo-3-oxo-5-methylhexanoate (**29**): IR (neat) 2130, 1730, 1660, 1450, 1385, and 1320 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.95 (d, 6 H, J = 6.0 Hz), 2.23 (m, 1 H), 2.52 (t, 1 H, J = 2.0 Hz), 2.75 (d, 2 H, J = 6.0 Hz), and 4.85 (d, 2 H, J = 2.0 Hz).

To a stirred solution containing 0.5 g (2.4 mmol) of **29** in 50 mL of dry benzene was added 10 mg of rhodium(II) acetate. The solution was heated at reflux for 3 h and was then concentrated under reduced pressure. The crude oil was purified to give 240 mg of a pale yellow oil that corresponded to a 1:1 mixture of 1-oxo-6-isobutyl-1*H*,3*H*-furo[3,4-*c*]furan (**30**) and 2-propynyl 2-oxo-4,4-dimethylcyclobutane-1-carboxylate (**31**). The products were separated by gas chromatography. Compound **30**: IR (neat) 1765, 1655, 1560, 1455, and 1235 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 0.95 (d, 6 H, J = 6 Hz), 2.19 (m, 1 H), 2.75 (d, 2 H, J = 6 Hz), 5.16 (d, 2 H, J = 1 Hz), and 7.16 (d, 1 H, J = 1 Hz); HRMS calcd for $C_{10}H_{12}O_3$ 180.0786, found 180.0786. Compound **31**: IR (neat) 2120, 1795, 1730, 1640, 1375, 1250, and 1140 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.36 (s, 3 H), 1.51 (s, 3 H), 2.46 (t, 1 H, J = 2 Hz), 2.90 (s, 2 H), 3.83 (s, 1 H), and 4.72 (d, 2 H, J = 2 Hz); HRMS calcd for $C_{10}H_{12}O_3$ 180.0786, found 180.0786.

2-Butynyl 2-Diazo-3-oxo-5-methylhexanonate (32). 2-Butynyl diazoacetate was prepared in a manner similar to that used for **8a** from 2-butyn-1-ol in 89% yield: IR (neat) 2115, 1715, 1655, 1435, 1305, and 1150 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.75 (t, 3 H, J = 2 Hz), 4.72 (q, 2 H, J = 2 Hz), and 4.85 (s, 1 H). This diazo compound was converted into **32** in a manner similar to that described for **29** in 85% yield: IR (neat) 2130, 1725, 1670, 1380, 1310, and 1215 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.02 (d, 6 H, J = 6 Hz), 1.93 (t, 3 H, J = 2 Hz), 2.21 (m, 1 H), 2.82 (d, 2 H, J = 6 Hz), and 4.85 (q, 2 H, J = 2 Hz). This compound was treated with rhodium(II) acetate in the normal fashion to give a 1:1.5 mixture of 1-oxo-4-methyl-6-isobutyl-1*H*,3*H*-furo[3,4-*c*]furan (**33**) and 2-butynyl 2-oxo-4,4-dimethylcyclobutane-1-carboxylate (**33**) in 80% yield. The products were separated by gas chromatography. Compound **33**: IR (neat) 1765, 1615, 1340, and 1130 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 0.93 (d, 6 H, J = 7.0 Hz), 2.12 (m, 1 H), 2.25 (s, 3 H), 2.65 (d, 2 H, J = 7.0 Hz), and 5.08 (s, 2 H); HRMS calcd for $C_{11}H_{14}O_3$ 194.0943, found 194.0943. Compound **34**: IR (neat) 1790, 1735, 1650, and 1250 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.36 (s, 3 H), 1.49 (s, 3 H), 1.82 (t, 3 H, J = 1 Hz), 2.92 (s, 2 H), 3.79 (s, 1 H), and 4.65 (q, 2 H, J = 1 Hz); HRMS calcd for $C_{11}H_{14}O_3$: 194.0943. Found: 194.0945.

2-Propynyl 3-diazo-2-oxoheptanoate (35) was prepared from diazo compound **9** in a manner similar to that used for **29** in 81% yield: IR (neat) 2150, 1730, 1660, 1390, 1310, and 1210 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.92 (t, 3 H, J = 7 Hz), 1.45 (m, 4 H), 2.50 (t, 1 H, J = 2 Hz), 2.85 (t, 2 H, J = 7 Hz), and 4.82 (d, 2 H, J = 2 Hz). This material was treated with rhodium(II) acetate in the normal fashion to give a 1:3 mixture of 1-oxo-6-butyl-1*H*,3*H*-furo[3,4-*c*]furan (**36**) and 2-propynyl 2-oxo-5-methylcyclopentane-1-carboxylate (**37**) in 77% yield. The two products were separated by gas chromatography. Compound **36**: IR (neat) 1760, 1635, 1450, and 1150 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 0.91 (t, 3 H, J = 6 Hz), 1.32 (m, 2 H), 1.75 (m, 2 H), 2.83 (t, 2 H, J = 6 Hz), 5.18 (d, 2 H, J = 1 Hz), and 7.17 (d, 1 H, J = 1 Hz); HRMS calcd for $C_{10}H_{12}O_3$ 180.0786, found 180.0786. Compound **37**: IR (neat) 2120, 1755, 1725, 1450, and 1180 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.20 (d, 3 H, J = 6 Hz), 1.48 (m, 2 H), 2.30 (m, 2 H), 2.45 (m, 1 H), 2.60 (m, 2 H), 2.81 (d, 1 H, J = 7 Hz), and 4.75 (m, 2 H); HRMS calcd for $C_{10}H_{12}O_3$ 180.0786, found 180.0785.

Rhodium(II) Acetate Catalyzed Cyclization of 2-Alkynyl Diazophenylsulfonylacetates. To a stirred solution containing

2.6 mL (36 mmol) of bromoacetic acid, 4 mL (54 mmol) of 2-butynol, and 150 mL of benzene was added 0.1 g of *p*-toluenesulfonic acid. The reaction flask was fitted with a Dean-Stark trap and was heated at reflux for 18 h. The mixture was concentrated under reduced pressure, and the residue was chromatographed on silica gel to give 6.2 g (90%) of 2-butynyl bromoacetate: IR (neat) 1750, 1430, and 1210 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.81 (t, 3 H, J = 2 Hz), 3.85 (s, 2 H), and 4.75 (q, 2 H, J = 2 Hz).

A mixture containing 1.0 g (5.2 mmol) of this acetate, 1.0 g (6.1 mmol) of sodium benzenesulfinate, and 50 mL of methanol was stirred at reflux for 16 h. The mixture was concentrated under reduced pressure, and the crude oil was redissolved in 20 mL of THF. To this solution was added 800 mg (6.6 mmol) of mesyl azide and 1.5 mL of triethylamine (11 mmol), and the mixture was stirred for 18 h at 25 °C. The solution was concentrated under reduced pressure, and the residue was purified to give 660 mg (45%) of 2-butynyl diazophenylsulfonyl acetate (**40**): mp 105–106 °C; IR ($CHCl_3$) 2120, 1710, 1585, 1450, 1365, and 1170 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.80 (t, 3 H, J = 2 Hz), 4.85 (q, 2 H, J = 2 Hz), 7.65 (m, 3 H), and 8.15 (m, 2 H). Anal. Calcd for $C_{12}H_{10}N_2O_4S$: C, 52.79; H, 3.62; N, 10.07. Found: C, 51.73; H, 3.63; N, 10.14.

To a stirred solution containing 1.6 g (6.4 mmol) of **40** and 100 mL of dry benzene was added 30 mg of rhodium acetate. The solution was heated at reflux for 1.5 h, and the mixture was concentrated under reduced pressure. The residue was purified by chromatography to give 860 mg (60%) of 2-oxo-3-(phenylsulfinyl)-4-acetyl-2*H*,5*H*-furan (**44**): IR (neat) 1770, 1675, 1560, 1325, 1170, and 1015 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.65 (s, 3 H), 5.02 (s, 2 H), and 7.45 (m, 5 H); HRMS calcd for ($M^+ - O$) $C_{12}H_{10}O_3S$ 234.0351, found 234.0350.

2-Oxo-3-(phenylsulfinyl)-4-benzoyl-2*H*,5*H*-furan (45). 3-Phenyl-2-propynyl diazophenylsulfonylacetate (**41**) was prepared in a manner similar to that outlined above from 3-phenyl-2-propynol in 40% yield: mp 84–85 °C; IR ($CHCl_3$) 2125, 1720, 1490, 1450, 1345, 1290, 1165, and 1070 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 5.00 (s, 2 H), 7.51 (m, 8 H), and 8.15 (m, 2 H). Anal. Calcd for $C_{17}H_{12}N_2O_4S$: C, 59.99; H, 3.56; N, 8.23. Found: C, 60.08; H, 3.59; N, 8.27. This diazo compound was converted into 2-oxo-3-(phenylsulfinyl)-4-benzoyl-2*H*,5*H*-furan (**45**) in 90% yield: mp 116–117 °C; IR ($CHCl_3$) 1765, 1660, 1595, 1185, 1090, and 1000 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 5.05 (s, 2 H), and 7.60 (m, 10 H). Anal. Calcd for $C_{17}H_{10}O_4S$: C, 65.80; H, 3.25. Found: C, 65.74; H, 3.19.

Rhodium(II) Acetate Catalyzed Cyclization of 1,4-Bis(2-diazo-3-oxobutoxy)-2-butyne (46). To a stirred solution containing 3.0 g (35 mmol) of 2-butyne-1,4-diol, 7.0 mL (87 mmol) of diketene, and 75 mL of THF was added 0.5 mL of triethylamine, and the mixture was stirred at 25 °C for 16 h. To this solution was added 10.5 g (87 mmol) of mesyl azide and 20 mL of triethylamine. After being stirred for 6 h, the solution was concentrated under reduced pressure and the residue was purified to give 8.2 g (77%) of 1,4-bis(2-diazo-3-oxobutoxy)-2-butyne (**46**): mp 80–81 °C; IR (neat) 2120, 1720, 1650, 1370, 1220, and 1060 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.45 (s, 6 H) and 4.95 (s, 4 H). Anal. Calcd for $C_{12}H_{10}N_4O_6$: C, 47.06; H, 3.29; N, 18.30. Found: C, 46.95; H, 3.32; N, 18.25.

To a stirred solution containing 1.0 g (3.3 mmol) of **46** and 100 mL of dry benzene was added 30 mg of rhodium acetate. The solution was heated at reflux for 2 h and the mixture was concentrated under reduced pressure. The resultant yellow oil was purified by chromatography to give 740 mg (90%) of 4-(2-oxo-3-acetyl-2*H*,5*H*-furan-4-yl)-2-oxo-3-acetyl-2*H*,5*H*-furan (**49**): IR (neat) 1770, 1680, 1610, 1370, 1290, and 1160 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.55 (s, 6 H), and 5.05 (s, 4 H); HRMS calcd for $C_{12}H_{10}O_6$ 250.0473, found 250.0472.

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Supplementary Material Available: ^1H or ^{13}C NMR spectra of **28**, **30**, **31**, **33**, **34**, **36**, **37**, **44**, and **49** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.