Synthesis of Nitrogen-Containing Polycycles via Rhodium(II)-Induced Cyclization–Cycloaddition and Insertion Reactions of *N*-(Diazoacetoacetyl)amides. Conformational Control of Reaction Selectivity

Michael P. Doyle,* Roland J. Pieters, Jack Taunton, and Hoan Q. Pho

Department of Chemistry, Trinity University, San Antonio, Texas 78284

Albert Padwa,* Donald L. Hertzog, and Laura Precedo

Department of Chemistry, Emory University, Atlanta, Georgia 30322

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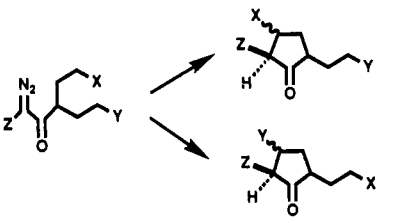
A series of diazoacetoacetamides, when treated with a catalytic quantity of a rhodium(II) carboxylate, were found to afford products derived from both a carbonyl ylide intermediate and intramolecular C–H insertion. With 3-(*N*-(diazoacetoacetyl)amino)propanoate derivatives, the rhodium(II)-catalyzed carbenoid reactions exhibit a strong preference for formation of a β-lactam ring. This is attributed to a conformational preference that juxtaposes the carbenoid center and the less sterically encumbered amide substituent and is consistent with an activating influence on the C–H bond adjacent to the amide nitrogen atom. Carbonyl ylide products derived from carbenoid cyclization onto the ester carbonyl group are also formed, and their relative yields are dependent on electronic influences from the bridging ligands of rhodium(II). Treatment of a series of cyclic diazoimides with rhodium(II) acetate resulted in cyclization of the rhodium carbenoid onto the adjacent imide carbonyl group to produce an isomünchnone dipole. Cyclization onto the imide carbonyl group occurs exclusively even when C–H insertion or aromatic substitution reactions of the carbenoid intermediate are favorable, and this selectivity is also attributed to conformational preferences that juxtapose the carbenoid center and imide carbonyl group. The isomünchnone dipole readily undergoes cycloaddition with several different dipolarophiles to give 1,3-dipolar cycloadducts. When acetylenic dipolarophiles were used as the trapping agents, the initial cycloadducts were found to undergo a [4 + 2]-cycloreversion, producing substituted furans in high yield. The generality of the method was demonstrated by varying the ring size of the cyclic imide. An analogous cyclization–cycloaddition reaction also occurred using diazoacetoacetyl-substituted ureas.

α-Diazocarbonyl compounds have found numerous applications in organic synthesis, and their use in either heterocyclic or carbocyclic ring formation is well precedented.[1-7] Intramolecular reactions involving either ylide generation or carbon–hydrogen insertion are facile processes that can be effectively used to design unique molecular constructions. Although free carbenes undergo these transformations, their lack of selectivity has limited their applications.[8] Only recently, with the utilization of rhodium(II) carboxylate catalysts, have these cyclization reactions become synthetically useful.

Intramolecular rhodium(II) carboxylate catalyzed carbenoid reactions exhibit an overwhelming preference for formation of five-membered rings.[9] Electronic factors have been reported to control selectivity for carbocyclic ring formation (Scheme I). Electron-donating substituents activate adjacent carbon–hydrogen bonds and electron-withdrawing substituents, even two atoms removed, deactivate carbon–hydrogen bonds in carbenoid insertion reactions.[9-11] Similar regioselectivity and electronic influences are known, but less well defined, with ylide generation in catalytic reactions of diazocarbonyl compounds.[12,13]

Scheme I



The factors responsible for selectivity in catalytic carbenoid reactions became less clear with recent reports that diazoamides undergo intramolecular carbon–hydrogen insertion to form β-lactams (eq 1).[14-16] The success of this

(1)

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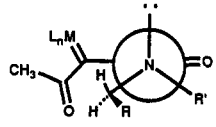
Table I. Competition between Ylide Generation and Carbon–Hydrogen Insertion as a Function of Rhodium(II) Catalyst from Decomposition of 5[a]

Rh_2L_4	isolated yield, %	relative yield, % 6	7	8
$Rh_2(pfb)_4$	97	22	17	61
$Rh_2(OAc)_4$	85	59	9	32
$Rh_2(acam)_4$	89	64	26	10

[a] Reactions were performed in refluxing benzene.

transformation was attributed to conformational preferences which placed the reacting C–H bond in close proximity to the carbenoid center (1).[15,16] Overlap of the nitrogen nonbonded electrons with the carbonyl π-system fixes the amide conformation so that the larger nitrogen substituent (R′) is preferentially oriented toward the carbonyl group, and the smaller substituent is placed in close proximity to the carbenoid carbon. In this way even highly reactive carbenoid intermediates can be effectively intercepted by intramolecular carbon–hydrogen bond insertion and, presumably, also by intramoleclar carbonyl ylide formation (2).



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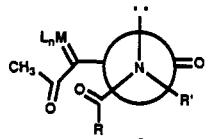

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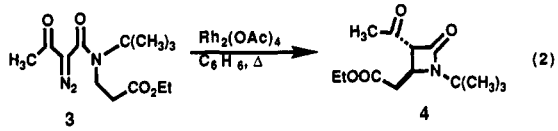
Results and Discussion

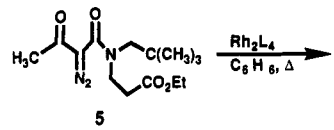
Carbon–Hydrogen Insertion. The importance of conformational influences can be readily seen in the results from intramolecular carbenoid reactions of diazoacetoacetamides. Decomposition of **3** in refluxing benzene, catalyzed by rhodium(II) acetate, forms β-lactam **4**, solely as the trans isomer, in nearly quantitative yield (eq 2).



(2)

3 4

Neither carbon–hydrogen insertion into the C–H bond of the *tert*-butyl group nor the position α to the ester functional group occurred even though both would have produced an ordinarily favored five-membered ring. This example stands in marked contrast to the results from catalytic decomposition of the *N*-neopentyl analogue of **3** from which both β- and γ-lactams (**6** and **7**) and, in addition, the carbonyl ylide derived product **8** (eq 3) are formed. By changing the catalyst from $Rh_2(pfb)_4$ (pfb = perfluorobutyrate)[17] through $Rh_2(OAc)_4$ to $Rh_2(acam)_4$ (acam = acetamide),[18] significant manipulation of the product distribution could be achieved (Table I). However, in no case could products from carbon–hydrogen insertion into the neopentyl methylene or methyl groups be identified as significant components in the reaction mixture (<3%). The formation of γ-lactam **7** is surprising in view of the deactivation reported to be associated with carbon–hydrogen insertion into the methylene group α to an ester functional group.[10] However, β-lactam **6** is the principal insertion product, and its formation is consistent



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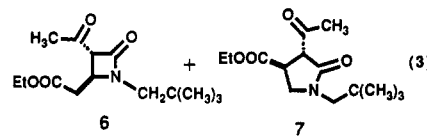

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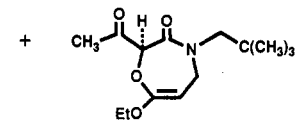
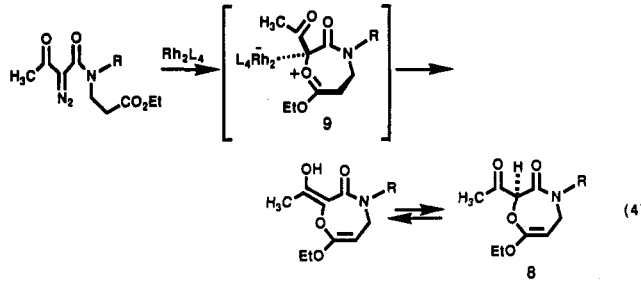


8

with an activating influence on the C–H bond adjacent to an amide nitrogen, even though this position is also assumed to be deactivated by the ester.

The major product from $Rh_2(pfb)_4$-catalyzed decomposition of **5** is **8**, which arises from ester carbonyl entrapment of the intermediate metal carbene. Its yield increases with the electron-withdrawing capabilities of the bridging ligands of the dirhodium(II) catalyst and is greatest with $Rh_2(pfb)_4$, whose derivative metal carbene has the highest oxophilicity.[19] Although precedented in both inter- and intramolecular reactions of carbenoid intermediates with ketones,[12] carbonyl ylide formation is not a common process with esters.[20] The uniqueness of the events leading to **8** can also be seen in the absence of a similar product from catalytic decomposition of **3** with $Rh_2(OAc)_4$.

If a free ylide intermediate was formed in these reactions, it should have been amenable to trapping by 1,3-dipolar addition. However, neither dimethyl acetylenedicarboxylate (DMAD) nor benzaldehyde, even when employed in a 10-fold molar excess relative to **5**, was successful in intercepting a carbonyl ylide. Instead, **8** was obtained in the same relative yield as from reactions performed in the absence of these dipolaraphiles. Thus, if a free ylide was formed, its lifetime must have been very short. Alternatively, **8** could be formed by a 1,6-hydrogen transfer (eq 4) of the metal stabilized ylide (**9**) that has its acetyl



(4)

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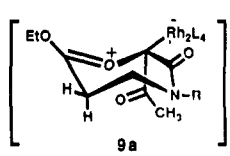
carbonyl group near the α-hydrogen of the ester (**9a**). This



9a

intermediate has support in results recently provided by Landgrebe and co-workers for enol ether formation from

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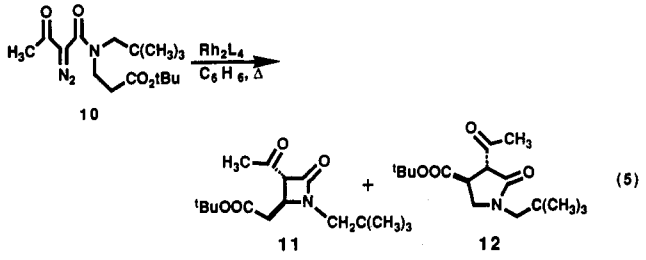
Table II. Competition between β- and γ-Lactam Formation from Decomposition of 10 as a Function of Rhodium(II) Catalyst[a]

		relative yield, %	
Rh_2L_4	isolated yield, %	11	12
$Rh_2(pfb)_4$	62	>95	<5
$Rh_2(OAc)_4$	83[b]	91	9
$Rh_2(acam)_4$	72	84	16

[a] Reactions were performed in refluxing benzene. [b] Includes 14% yield of the ylide derived product that is the *tert*-butoxy analogue of 8.

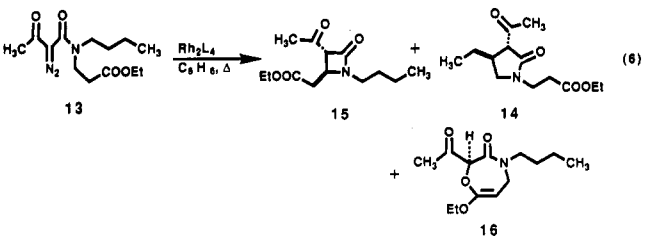
carbonyl ylides in catalytic reactions of ethyl diazoacetate with ketones[21] and in observations of catalyst dependent stereoselectivities made by Roskamp and Johnson for cyclobutanone formation through oxygen ylides.[13b]

The enormous difference in products resulting from the stable structural changes in reactants 3 and 5 suggested the need to determine the influence of ester and amide substituents on carbonyl ylide formation. Replacement of the ethyl ester substituent of 5 by a *tert*-butyl ester (10) resulted in the formation of 11 and 12 without any evidence for the *tert*-butoxy analogue of 8 from reactions catalyzed by $Rh_2(pfb)_4$ or $Rh_2(acam)_4$ (eq 5), although this



carbonyl ylide derived product was obtained in 14% yield from $Rh_2(OAc)_4$-catalyzed reactions of 10. The dependence of the relative yields for the β- and γ-lactams derived from 10 on the bridging ligands of the dirhodium(II) catalyst (Table II) is similar to that observed for 5. The absence of the *tert*-butoxy analogue of 8 is consistent with steric crowding of the carbonyl group in the *tert*-butyl ester that inhibits effective carbonyl ylide formation.

Replacement of the *N*-*tert*-butyl substituent of 3 by an *N*-*n*-butyl substituent (13) provides further insight into the structural influences on the carbenoid. The comparable sizes of the *n*-butyl and β-propionate substituents suggest that there should be a nearly equal distribution of products resulting from intramolecular reactions with both amide substituents. This indeed is what is observed (eq 6). γ-Lactam 14 is the sole product from carbon–



hydrogen insertion into the *n*-butyl substituent and accounts for 61–71% of the products (Table III). Intramolecular reactions on the β-propionate substituent occur by both carbon–hydrogen insertion (15) and carbonyl ylide generation (16). Carbonyl ylide generation dominates, to the exclusion of 15, in reactions catalyzed by $Rh_2(pfb)_4$.

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Table III. Competition between Ylide Generation and Carbon–Hydrogen Insertion from Decomposition of 13 as a Function of Rhodium(II) Catalyst[a]

		relative yield, %		
Rh_2L_4	isolated yield, %	14	15	16
$Rh_2(pfb)_4$	90	61	0	39
$Rh_2(OAc)_4$	93	62	7	31
$Rh_2(acam)_4$	91	71	14	15

[a] Reactions were performed in refluxing benzene.

Consistent with our model of conformational preferences for carbenoid reactions with diazoamides, changing the bridging rhodium(II) ligands does not substantially alter the product distribution from reactions with the *n*-butyl (14) and β-propionate (15 + 16) substituents of the amide.

Metal carbenes generated from diazoacetoacetamides clearly exhibit conformational preferences that juxtapose the carbenoid center and the less sterically encumbered amide substituent. A carbon–hydrogen bond α to the amide nitrogen is activated for insertion, especially when the β-C–H bond is deactivated (eq 6), but an ester group that is further removed from nitrogen can compete for entrapment of the reactive metal carbene. These same controlling factors should be evident in other carbenoid processes.

Carbonyl Ylide Generation. Ylide formation as a result of carbene interaction with the unshared electron pair of heteroatoms has been extensively studied.[2] In contrast to the abundant literature dealing with the addition of a rhodium carbenoid intermediates onto the oxygen end of a keto group,[22-24] little was known about the interaction of the metal carbenoid with other carbonyl groups when we started our work in this area.[25] Several immediate questions were posed: (1) will a nucleophilic amide or imide functionality cyclize more or less efficiently than the keto group to give the 1,3-dipole; (2) to what extent will the cyclization be dependent on the length of the tether separating the carbenoid center and the neighboring carbonyl group; (3) since diazoketones are reactive dipoles, will the presence of an activated π-bond be subject to uncontrollable cycloaddition across the diazo group to produce a pyrazoline cycloadduct? In addition, given the propensity of metal carbenoids to undergo addition and insertion reactions,[1-3] would carbonyl ylide generation compete effectively with alternative transformations when they were possible?

Cyclic diazoimides 17–20 were easily prepared in high yield by heating the appropriate cyclic amide with 2,2,6-trimethyl-4*H*-1,3-dioxen-4-one[26] in xylene at 140 °C. The resulting *N*-(acetoacetyl)amide was treated with mesyl azide/triethylamine in the usual way to give the diazoimides.[27] A sample of cyclic diazoimide 17 was allowed to react with rhodium acetate (80 °C) in benzene, and the initially formed rhodium carbenoid cyclized onto the ad-

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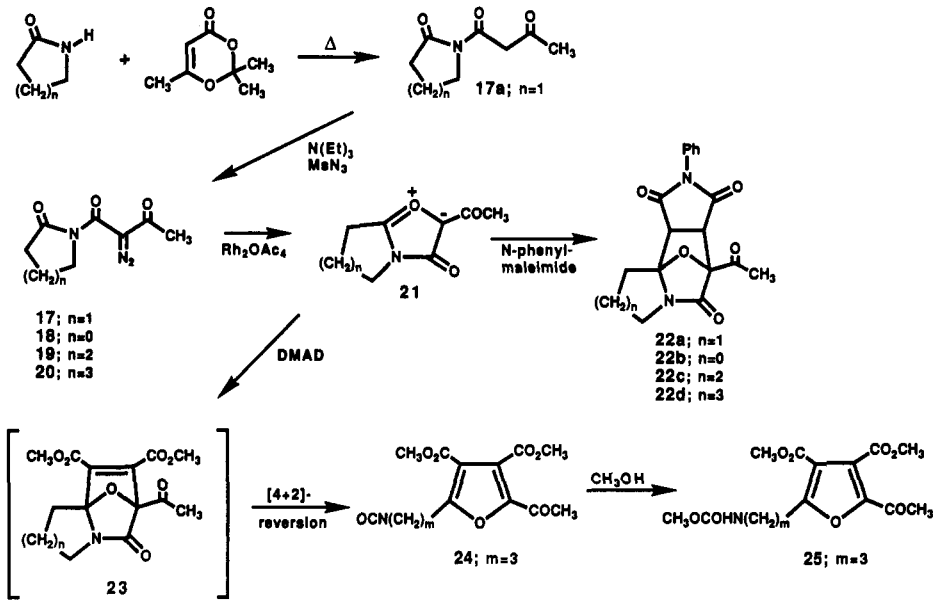
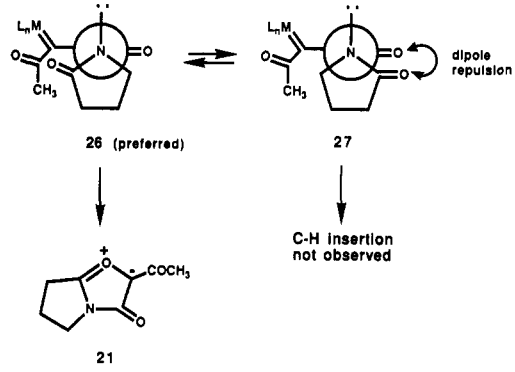
Scheme II



jacent imide carbonyl group to produce an isomünchnone dipole (**21**).[28] This species readily undergoes 1,3-dipolar cycloaddition with *N*-phenylmaleimide to afford the expected dipolar cycloadduct **22** as a 1.2:1 mixture of exo and endo isomers in 78% yield without evidence of products from potentially competitive C–H insertion. The generality of the method was demonstrated by varying the cyclic imide so as to probe any geometric effects of ring size on the outcome of the cyclization–cycloaddition reaction. The ring size was reduced to a four-membered ring (**18**; $n = 0$) and enlarged to a six (**19**; $n = 2$) and seven (**20**; $n = 3$) membered ring. In all cases, high yields (i.e., 70–90%) of the expected cycloadduct derived from *N*-phenylmaleimide were obtained. Interestingly, the cyclic cases where $n = 1$ and $n = 3$ (i.e., **17** and **20**) showed little exo/endo selectivity, but the cases of $n = 0$ and $n = 2$ (**18** and **19**) resulted in a single stereoisomer (Scheme II).

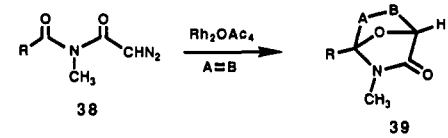
When DMAD was used as the trapping dipolarophile, the expected cycloadduct was not isolated. Instead, furanoisocyanate **24** ($m = 3$) was the only product formed in 85% yield. This is the result of a subsequent [4 + 2]cycloreversion of the initially formed cycloadduct under the reaction conditions. Isocyanate **24** was characterized as its urethane derivative **25** by reaction with methanol. Recently, Maier and Schöffling have found that acetylenic isomünchnones formed by the rhodium acetate catalyzed decompoasition of diazoacetyl *N*-(methylalkynyl)amide derivatives undergo an analogous intramolecular cycloaddition.[29] The initial cycloadduct could not be isolated since it undergoes spontaneous fragmentation under the reaction conditions to give annulated furans in good yield.

It should be noted that with diazoimides **17–20** no detectable quantities of a β-lactam were present in the crude reaction mixture. Thus, the initially formed rhodium carbenoid prefers to cyclize onto the adjacent amide carbonyl group rather than undergo intramolecular carbon-hydrogen insertion as was encountered with diazoacetoacetamides **3, 5, 10, and 13**. More than likely the preferred rhodium carbenoid (i.e., conformer **26**) is the one which avoids an unfavorable dipole repulsion between the two amido groups (i.e., conformer **27**).



The conformational rigidity imposed by the cyclic imide ring was demonstrated to be inconsequential for carbonyl ylide formation by carrying out the tandem cyclization–cycloaddition sequence using acyclic imides **28** and **29**. Both substrates readily reacted with $Rh_2(OAc)_4$ in the presence of DMAD to give cycloadducts **30** and **31** in 82% and 86% yields, respectively. Similarly, reaction with *N*-phenylmaleimide afforded cycloadducts **32** and **33** in 76 and 65% yield as a mixture of exo and endo isomers (see the Experimental Section). Once again, products from C–H insertion into *N*-methyl or *N*-ethyl substituents were not observed (see Scheme III).

Since we were interested in the synthetic utility of these rhodium-catalyzed cyclizations, we also undertook a study of the rhodium-catalyzed behavior of the simpler diazoacetyl system **38**. Deacylation of the *N*-diazoacetoacetyl compounds was carried out in high yield according to the general method of Sundberg and Pearce.[30] We found that under the same reaction conditions used for the *N*-diazoacetoacetyl compounds, the yields of cycloadducts **39** were



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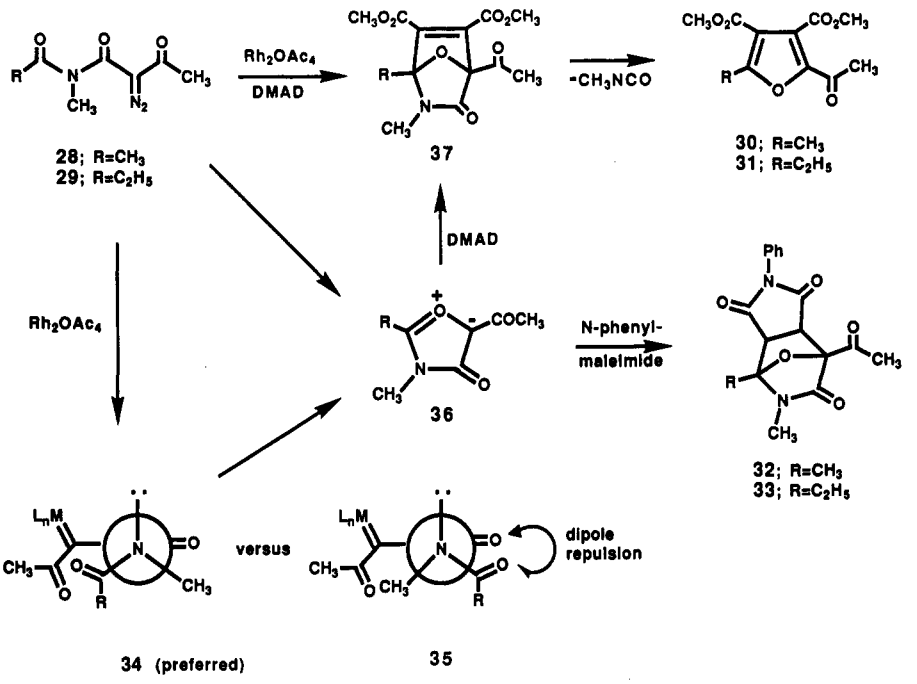
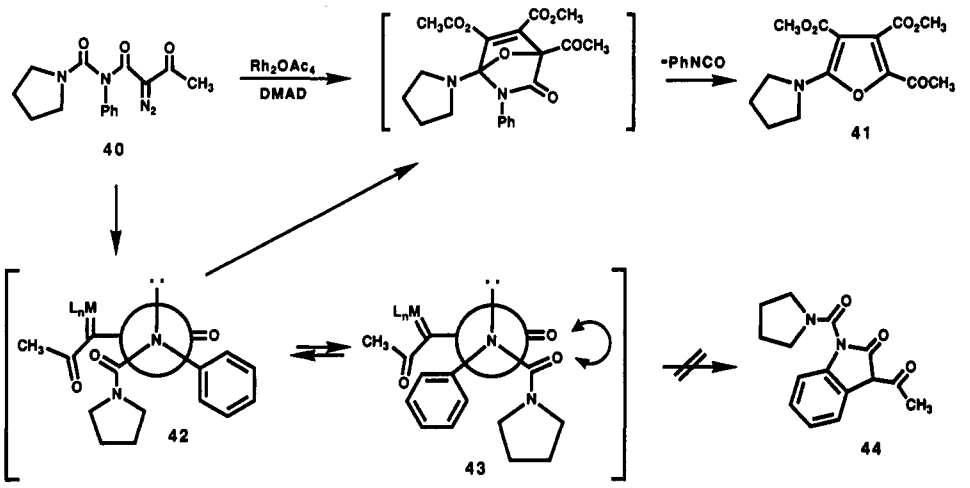
Scheme III



Scheme IV

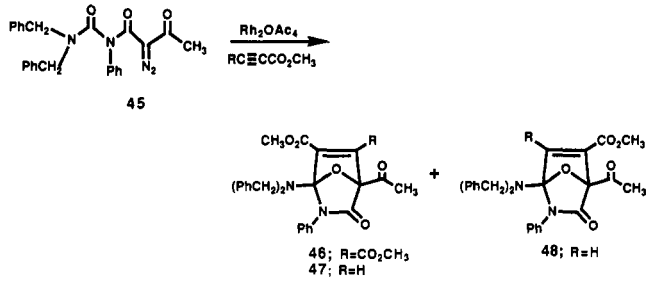


significantly diminished. One possible explanation for the differing reactivity of the *N*-diazoacetyl system is the inherent decrease in electrophilic character conferred upon the intermediate rhodium carbenoid when the diazo carbon bears a hydrogen atom rather than an acetyl group. This decrease in electrophilicity may alter the rate of carbenoid attack on the remote carbonyl group to the point where an alternative reaction can occur. Alternatively, the preferred conformation of the intermediate rhodium carbenoid may not be the one that is favorable to carbonyl ylide formation.

As an extension of our studies in this area, we have also examined the rhodium-catalyzed behavior of the closely related diazoacetoacetyl urea **40**. Exposure of **40** to the rhodium carboxylate catalyst in benzene with DMAD afforded furan **41** in excellent yield. This material can be rationalized as being derived by a [4 + 2]-cycloreversion of the initially formed dipolar cycloadduct. Although electrophilic aromatic substitution that would yield 2-(3*H*)-indolinone **44** is ordinarily a facile process in $Rh_2(OAc)_4$-catalyzed reactions of *N*-phenyldiazoacetoacetamides,[31] this product was not formed by catalytic decomposition of **40** (Scheme (IV). Once again, the preferred conformation of the intermediate rhodium carbenoid (**42**) is the one that avoids an unfavorable dipole repulsion between the two amido groups (**43**).

Interestingly, treatment of the structurally related dibenzyl(diazoacetoacetyl)urea **45** with DMAD afforded cycloadduct **46** derived from the isomüchnone dipole. Similar results were also obtained by using methyl propiolate as the dipolarophile. In this case, a 2:1 mixture of two regioisomers (**47** and **48**) was obtained in 75% overall yield. With the dibenzylamino-substituted urea system (i.e., **45**), the cycloadduct derived from the isomüchnone dipole is stable enough to be isolated. With the other systems (**23** and **37**), however, loss of methyl or phenyl isocyanate occurred rapidly and only the furan derived from a [4 + 2]-cycloreversion was obtained. The regiochemistry encountered in the reaction of **45** with methyl propiolate can be rationalized on the basis of FMO considerations.[32,33] For carbonyl ylides, the HOMO of the

(31) Doyle, M. P.; Shanklin, M. S.; Pho, H. Q.; Mahapatro, S. N. *J. Org. Chem.* **1988**, *53*, 1017.



dipole is dominant for reactions with electron-deficient dipolarophiles such as methyl propiolate.[34] MNDO calculations on the isomüchnone derived from **45** clearly indicate that the largest coefficient in the HOMO resides on the carbon bearing the acetyl group. This site becomes linked with the less substituted carbon of the acetylenic group, thereby accounting for the regiochemical results.

In conclusion, the facility with which the rhodium(II)-catalyzed cyclization–cycloaddition and insertion reaction of *N*-(diazoacetoacetyl)amides occurs makes these processes particularly attractive for the synthesis of nitrogen-containing polycycles. The controlling features of these transformations include electronic and steric interactions that define the preferred conformation of the reactive rhodium(II) carbenoid. Dipolar repulsion between two amido carbonyl groups favors that conformation in which the amide carbonyl group two atoms removed from the original diazo carbon is oriented in close proximity to the electrophilic metal carbene center (e.g., **26**, **34**, **42**). Similarly, bulky alkyl groups on the amide nitrogen are preferentially oriented in close proximity to the sterically less demanding carbonyl group in the metal carbene conformation (e.g. **1**), which allows positioning of carbon–hydrogen bonds in the less bulky alkyl group adjacent to the reactive carbenoid center. We are continuing to explore the scope and mechanistic details of these rhodium-catalyzed processes.

Experimental Section

Melting points are uncorrected. Infrared spectra were run on dispersive or FT instruments. Proton NMR spectra were obtained from 90 or 300 MHz spectrometers, and ^{13}C NMR spectra were recorded at 75 MHz. Microanalyses were performed at Atlanta Microlabs, Atlanta, GA, or at Texas Analytical Laboratories, Inc. Mass spectra were determined at an ionizing voltage of 70 eV. $Rh_2(pfb)_4$[17] and $Rh_2(acam)_4$[18] were synthesized by acetate displacement from stock $Rh_2(OAc)_4$.

General Procedure for the Synthesis of Diazoacetoacetamides. To 28 mmol of freshly distilled diketene in 30 mL of anhydrous THF, cooled in an ice bath, was added 25 mmol of the 3-(*N*-alkylamino)propionate ester in 30 mL of THF dropwise over a 30-min period. (The reverse addition results in the product from an intramolecular base-induced Claisen condensation.) The resulting solution was allowed to warm to room temperature and maintained with stirring at that temperature for 12 h. Ether (30 mL) was added, and this solution was extracted with 50 mL of a saturated solution of NH_4Cl that was diluted with 50 mL of water. After extracting the aqueous layer twice with 30-mL portions of ether, the combined ether fraction was washed with 30 mL of a saturated NaCl solution, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to yield a pale yellow liquid that was then dissolved in 45 mL of anhydrous CH_3CN to which was added 27 mmol of mesyl azide. Triethylamine (50 mmol) in 15 mL of CH_3CN was added dropwise over a 30-min period, and the resulting deep orange solution was maintained with stirring at room temperature for 12 h. This solution was then poured into 70 mL of water and extracted three times with 30-mL portions of ether and/or ethyl acetate. The combined ether fraction was washed with 50 mL of saturated NaCl, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to furnish the crude diazo compound which was purified by flash chromatography on silica gel using either hexane–ethyl acetate or pentane–ether mixtures as the eluent. The following diazoacetoacetamides were produced in this manner:

Ethyl 3-(*N*-*tert*-butyl-*N*-(diazoacetoacetyl)amino)propanoate (3): yellow oil, 62% overall yield: IR (neat) 2102 (C=N_2), 1733 (ester C=O), 1651, and 1647 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 4.13 (q, J = 7.1 Hz, 2 H), 3.69 (t, J = 7.0 Hz, 2 H), 2.59 (t, J = 7.0 Hz, 2 H), 2.30 (s, 3 H), 1.46 (s, 9 H), and 1.24 (t, J = 7.1 Hz, 3 H).

Ethyl 3-(*N*-neopentyl-*N*-(diazoacetoacetyl)amino)propanoate (5): yellow oil, 64% overall yield; IR (neat) 2104 (C=N_2), 1732 (ester C=O), 1654, and 1636 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 4.13 (q, J = 7.1 Hz, 2 H), 3.70 (t, J = 6.7 Hz, 2 H), 3.24 (s, 2 H), 2.60 (t, J = 6.7 Hz, 2 H), 2.31 (s, 3 H), 1.26 (t, J = 7.1 Hz, 3 H), and 0.94 (s, 9 H).

***tert*-Butyl 3-(*N*-neopentyl-*N*-(diazoacetoacetyl)amino)propanoate (10)**: yellow oil, 64% overall yield; IR (neat) 2104 (C=N_2), 1727 (ester C=O), 1654, and 1637 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.66 (t, J = 6.7 Hz, 2 H), 3.25 (s, 2 H), 2.50 (t, J = 6.7 Hz, 2 H), 2.31 (s, 3 H), 1.43 (s, 9 H), and 0.94 (s, 9 H).

Ethyl 3-(*N*-*n*-butyl-*N*-(diazoacetoacetyl)amino)propanoate (13): yellow oil, 92% overall yield; IR (neat) 2105 (C=N_2), 1732 (ester C=O), and 1634 (amide C=O) cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 4.14 (q, J = 7.1 Hz, 2 H), 3.63 (t, J = 7.0 Hz, 2 H), 3.31 (t, J = 7.6 Hz, 2 H), 2.64 (t, J = 7.0 Hz, 2 H), 2.32 (s, 3 H), 1.57 (quin, J = 7.6 Hz, 2 H), 1.31 (sex, J = 7.6 Hz, 2 H), 1.27 (t, J = 7.1 Hz, 3 H), and 0.93 (t, J = 7.3 Hz, 3 H).

Catalytic Decomposition of Ethyl 3-(*N*-*tert*-Butyl-*N*-(diazoacetoacetyl)amino)propanoate (3). A solution of 283 mg of **3** (1.00 mmol) and 4.4 mg of rhodium(II) acetate (1.0 mol %) in 10 mL of benzene was heated at reflux for 3 h. The resulting solution was filtered through a plug of neutral alumina to separate the $Rh_2(OAc)_4$, and benzene was removed under reduced pressure. The resulting residue (218 mg) consisted of a single monomeric product which was distilled (bp 121 °C at 0.1 Torr) to give β-lactam **4** as a colorless oil: IR (neat) 1749 (amide C=O), 1734 (ester C=O), and 1714 (ketone C=O) cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 4.23 (ddd, J = 9.3, 3.8, 2.1 Hz, 1 H), 4.07 and 4.06 (2 q, J = 7.2, 7.2 Hz, 2 H), 3.90 (d, J = 2.1 Hz, 1 H),[35] 2.85 (dd, J = 15.6, 3.8 Hz, 1 H), 2.50 (dd, J = 15.6, 9.3 Hz, 1 H), 2.22 (s, 3 H), 1.27 (s, 9 H), and 1.15 (t, J = 7.2 Hz, 3 H). Anal. Calcd for $C_{13}H_{21}NO_4$: C, 61.12; H, 8.31; N, 5.49. Found: C, 61.03; H, 8.26; N, 5.52.

Catalytic Decomposition of Ethyl 3-(*N*-Neopentyl-*N*-(diazoacetoacetyl)amino)propanoate (5). A solution of 297 mg of **5** (1.00 mmol) and 10.6 mg of $Rh_2(pfb)_4$ (1.0 mol %) in 10 mL of benzene was heated at reflux for 3 h. The resulting solution was subjected to flash chromatography on silica gel (ethyl acetate), and the solvent was removed under reduced pressure to reveal a mixture of three products (229 mg) that was separated on silica gel by radial chromatography (1:1 hexane–ethyl acetate). After two passes the major fraction was a white crystalline solid (mp 85 °C) that was identified as **8** by spectral analysis: IR (KBr) 1736 (ester C=O), 1690, and 1642 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 4.97 (dd, J = 4.2, 3.2 Hz, 1 H), 4.80 (s, 1 H), 4.17 (dd, J = 17.0, 3.2 Hz, 1 H), 3.97 (dd, J = 17.0, 4.2 Hz, 1 H), 3.82 (q, J = 7.0 Hz), and 3.79 (q, J = 7.0 Hz) for CH_2O, 3.57 (d, J = 13.6 Hz, 1 H), 3.08 (d, J = 13.6 Hz, 1 H), 2.27 (s, CH_3), 1.33 (t, J = 7.0 Hz, 3 H), and 0.98 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 204.6, 167.4, 150.2, 93.2, 79.2, 63.8, 59.2, 48.9, 34.4, 28.5, 24.8, and 14.2. Anal. Calcd for $C_{14}H_{23}NO_4$: C, 62.42; H, 8.61; N, 5.20. Found: C, 62.35; H, 8.66; N, 5.23.

A second fraction was a colorless oil that was identified as β-lactam **6** by spectral analysis: IR (neat) 1757 (amide C=O),

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1735 (ester C=O), and 1715 (ketone C=O) cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 4.38 (ddd, J = 7.8, 5.0, 2.0 Hz, 1 H), 4.15 (q, J = 7.1 Hz, 2 H), 4.04 (d, J = 2.0 Hz, 1 H), 3.25 (d, J = 14.3 Hz, 1 H), 2.80 (dd, J = 15.7, 5.0 Hz, 1 H), 2.58 (d, J = 14.3 Hz, 1 H), 2.55 (dd, J = 15.7, 7.8 Hz, 1 H), 2.33 (s, 3 H), 1.25 (t, J = 7.1 Hz, 3 H), and 0.94 (s, 9 H). Anal. Calcd for $C_{14}H_{23}NO_4$: C, 62.42; H, 8.61; N, 5.20. Found: C, 62.24; H, 8.66; N, 5.17.

The minor fraction was identified as γ-lactam **7** by spectral analysis: NMR ($CDCl_3$, 300 MHz) δ 4.18 (q, J = 7.1 Hz, 2 H), 3.93 (d, J = 6.1 Hz, 1 H), 3.78 (ddd, J = 7.9, 6.6, 6.1 Hz, 1 H), 3.70 (dd, J = 9.8, 7.9 Hz, 1 H), 3.60 (dd, J = 9.8, 6.6 Hz, 1 H), 3.04 (s, 2 H), 2.49 (s, 3 H), 1.27 (t, J = 7.1 Hz, 3 H), and 0.93 (s, 9 H).

Similar reactions were performed with $Rh_2(OAc)_4$ and $Rh_2(acam)_4$. The product distributions were determined on the reaction mixture prior to chromatographic separation by integration of characteristic product NMR absorptions and by GC (SPB-5 column) following removal of the catalyst. Variability in relative product yields was ±5%.

Attempted Trapping of Carbonyl Ylide (9) with Dimethyl Acetylenedicarboxylate. A benzene solution (10 mL) containing 297 mg of **5** (1.0 mmol), 10.6 mg of $Rh_2(pfb)_4$ (1.0 mol %), and 284 mg of dimethyl acetylenedicarboxylate (DMAD) was heated at reflux for 3 h, and the resulting solution was chromatographed as previously described. No change in the relative yields of products **4–6** was observed (66% **8**, 17% **6**, and 17% **7**). When this reaction was repeated in the presence of 10 equiv of DMAD (1.42 g), the same results were obtained, and there was no evidence of any cycloaddition product. Similar results were obtained from a reaction performed in the presence of 10 equiv of benzaldehyde (55% **8**, 28% **6**, and 17% **7**).

Catalytic Decomposition of *tert*-Butyl 3-(*N*-Neopentyl-*N*-(diazoacetoacetyl)amino)propanoate (10). A solution of 325 mg of **10** (1.00 mmol) and 10.6 mg of $Rh_2(pfb)_4$ (1.0 mol %) in 10 mL of benzene was heated at reflux for 14 h. Following flash chromatography to remove the catalyst and both GC and NMR analyses of the product mixture, the resulting solution was subjected to radial chromatography on silica gel (1:3 ethyl acetate–hexane) to separate the two reaction components. Similar reactions were performed with $Rh_2(OAc)_4$ and $Rh_2(acam)_4$. The major product was a colorless oil that was identified as β-lactam **11** by spectral analysis: IR (neat) 1760 (amide C=O), 1728 (ester C=O), and 1715 (ketone C=O) cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 4.35 (ddd, J = 7.8, 4.7, 2.1 Hz, 1 H), 4.05 (d, J = 2.1 Hz, 1 H), 3.25 (d, J = 14.3 Hz, 1 H), 2.71 (dd, J = 15.4, 4.7 Hz, 1 H), 2.57 (d, J = 14.3 Hz, 1 H), 2.48 (dd, J = 15.4, 7.8 Hz, 1 H), 2.34 (s, 3 H), 1.44 (s, 9 H), and 0.95 (s, 9 H). Anal. Calcd for $C_{16}H_{27}NO_4$: C, 64.62; H, 9.15; N, 4.71. Found: C, 64.53; H, 9.28; N, 4.63.

The minor fraction was identified as γ-lactam **12** by spectral analysis: IR (neat) 1728 and 1694 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.89 (d, J = 6.3 Hz, 1 H), 3.72 (dd, J = 8.1, 5.8 Hz, 1 H), 3.65 (ddd, J = 6.2, 5.8, 4.7 Hz, 1 H), 3.59 (dd, J = 8.1, 4.7 Hz, 1 H), 3.03 (s, 2 H), 2.47 (s, 3 H), 1.45 (s, 9 H), and 0.93 (s, 9 H).

In reactions performed with $Rh_2(OAc)_4$, the *tert*-butoxy analogue of **8** was observed by NMR spectroscopy in the reaction mixture prior to chromatography on neutral alumina to remove the catalyst: NMR ($CDCl_3$, 300 MHz) δ 5.18 (t, J = 3.8 Hz, 1 H), 4.71 (s, 1 H), 4.10 (dd, J = 17.1, 3.5 Hz, 1 H), 3.99 (dd, J = 17.1, 3.7 Hz, 1 H), 3.48 (d, J = 13.5 Hz, 1 H), 3.12 (d, J = 13.5 Hz, 1 H), 2.23 (s, 3 H), 1.37 (s, 9 H), and 0.97 (s, 9 H). However, this product was absent following chromatography, and attempts to achieve its isolation were not successful. Similar analyses of reaction mixtures performed with $Rh_2(acam)_4$ or $Rh_2(pfb)_4$ showed none of the NMR absorptions expected for this product.

Catalytic Decomposition of Ethyl 3-(*N*-*n*-Butyl-*N*-(diazoacetoacetyl)amino)propanoate (13). A solution of 283 mg of **13** (1.00 mmol) and 10.6 mg of $Rh_2(pfb)_4$ (1.0 mol %) in 10 mL of benzene was heated at reflux for 3 h. Following flash chromatography to remove the catalyst and both GC and NMR analyses of the product mixture, the resulting solution was distilled (bp 160–170 °C at 0.03 Torr) and then subjected to radial chromatography on silica gel (3:47:50 methanol–ether–pentane) to separate the three reaction components. The major fraction was a colorless oil that was identified as γ-lactam **14** by spectral analysis: NMR ($CDCl_3$, 300 MHz) δ 4.18 (q, J = 7.2 Hz, 2 H), 3.55 (dd, J = 9.6, 8.2 Hz, 1 H), 3.55 (t, J = 6.8 Hz, 2 H), 3.23 (d, J = 7.3 Hz, 1 H), 3.00 (dd, J = 9.6, 6.2 Hz, 1 H), 2.73 (sex, J = 7.1 Hz, 1 H), 2.54 (t, J = 6.8 Hz, 2 H), 2.40 (s, 3 H), 1.45 (quin, J = 7.2 Hz, 1 H), 1.43 (quin, J = 7.2 Hz, 1 H), 1.25 (t, J = 7.2 Hz, 3 H), and 0.89 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 203.4, 171.3, 169.6, 61.8, 60.6, 51.3, 38.9, 34.9, 32.3, 30.1, 26.8, 14.0, and 11.3. Anal. Calcd for $C_{13}H_{21}NO_4$: C, 61.12; H, 8.31; N, 5.49. Found: C, 60.89; H, 8.20; N, 5.46.

A second fraction was a colorless oil that was identified as β-lactam **15** by spectral analysis: NMR ($CDCl_3$, 300 MHz) δ 4.31 (dt, J = 6.1, 2.2 Hz, 1 H), 4.15 (q, J = 7.1 Hz, 2 H), 3.99 (d, J = 2.2 Hz, 1 H), 3.42 (dt, J = 15.5, 7.7 Hz, 1 H), 3.29 (dt, J = 15.5, 7.5 Hz, 1 H), 2.66 (dd, J = 14.9, 6.1 Hz, 1 H), 2.60 (dd, J = 14.9, 6.0 Hz, 1 H), 2.31 (s, 3 H), 1.5–1.3 (m, 4 H), 1.24 (t, J = 7.1 Hz, 3 H), and 0.87 (t, J = 7.3 Hz, 3 H).

A third minor fraction was also a colorless oil that was identified as **16** by spectral analysis: IR (neat) 1735 (ester C=O), 1694, and 1651 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 5.00 (t, J = 3.6 Hz, 1 H), 4.75 (s, 1 H), 4.03 (dd, J = 7.2, 3.4 Hz, 1 H), 3.95 (dd, J = 17.2, 3.7 Hz, 1 H), 3.82 (q, J = 7.1 Hz), and 3.79 (q, J = 7.0 Hz) for CH_2O, 3.53 (dt, J = 13.4, 7.5 Hz, 1 H), 3.42 (dt, J = 13.4, 7.4 Hz, 1 H), 2.23 (s, 3 H), 1.59 (quin, J = 7.4 Hz, 2 H), 1.41–1.26 (m, 2 H), 1.31 (t, J = 7.0 Hz, 3 H), and 0.93 (t, J = 7.2 Hz, 3 H).

General Procedure for Synthesis of Diazo Imides. A variation of the procedure described by Kato and co-workers was used to prepare the keto amides.[36] A solution containing 30 mmol of the appropriate amide and 36 mmol of 2,2,6-trimethyl-1,3-dioxen-4-one in 30 mL of xylene was heated at reflux under N_2 for 2 h. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography with an ethyl acetate–hexane mixture as the eluent. To a solution containing 2 mmol of the appropriate keto amide and 2.2 mmol of mesyl azide in 5 mL of CH_3CN was added 4.0 mmol of Et_3N under a nitrogen atmosphere at room temperature. After the mixture was stirred for 3 h, the solvent was removed under reduced pressure and the residue was subjected to silica gel chromatography with an ethyl acetate–hexane mixture as the eluent. The diazo compounds were too labile to obtain proper elemental analyses. In this manner the following compounds were obtained.

1-(1,3-Dioxobutyl)-2-pyrrolidinone (17a): colorless oil, 89% yield; IR (neat) 2990, 2910, 1750, 1690, 1630, 1585, 1560, 1400, 1370, 1330, 1246, 1190, 1170, and 1025 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.97 (m, 2 H), 2.20 (s, 3 H), 2.50 (t, 2 H, J = 8.0 Hz), 3.75 (t, 2 H, J = 7.0 Hz), and 3.90 (s, 2 H). **1-(2-Diazo-1,3-dioxobutyl)-2-pyrrolidinone (17)**: pale yellow crystals; mp 51–52 °C; 88% yield; IR ($CHCl_3$) 3005, 2910, 2150, 1740, 1655, 1645, 1360, 1320, 1235, and 1190 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.00–2.20 (m, 2 H), 2.47 (s, 3 H), 2.60 (t, 2 H, J = 8.0 Hz), and 3.85 (t, 2 H, J = 7.0 Hz).

1-(1,3-Dioxobutyl)-2-azetidinone (18a): yellow oil, 81% yield; IR (neat) 2995, 2910, 1785, 1635, 1420, 1355, 1315, 1195, 1160, and 1050 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.20 (s, 3 H), 3.10 (t, 2 H, J = 6.0 Hz), 3.62 (t, 2 H, J = 6.0 Hz), and 3.81 (s, 2 H). **1-(2-Diazo-1,3-dioxobutyl)-2-azetidinone (18)**: yellow oil, 62% yield; IR (neat) 2980, 2920, 2140, 1790, 1710, 1660, 1340, 1300, 1225, 1120, and 1050 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.52 (s, 3 H), 3.12 (t, 2 H, J = 6.0 Hz), and 3.83 (t, 2 H, J = 6.0 Hz).

1-(1,3-Dioxobutyl)-2-piperidinone (19a): colorless oil, 72% yield; IR (neat) 2980, 2890, 1725, 1695, 1480, 1465, 1390, 1295, 1265, 1195, and 1155 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.62–2.00 (m, 4 H), 2.15 (s, 3 H), 2.32–2.67 (m, 2 H), 3.59–3.85 (m, 2 H), and 4.00 (s, 2 H). **1-(2-Diazo-1,3-dioxobutyl)-2-piperidinone (19)**: yellow crystals; mp 79–80 °C; 80% yield; IR ($CHCl_3$) 3030, 2970, 2140, 1690, 1665, 1395, 1365, 1320, 1290, 1270, and 1175 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.80–1.95 (m, 4 H), 2.47 (s, 3 H), 2.55 (t, 2 H, J = 6.5 Hz), and 3.69 (t, 2 H, J = 5.5 Hz).

1-(1,3-Dioxobutyl)hexahydro-2*H*-azepin-2-one (20a): colorless oil, 79% yield; IR (neat) 2940, 2870, 1725, 1690, 1680, 1395, 1360, 1185, 1150, 970, and 885 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.51–1.80 (m, 6 H), 2.22 (s, 3 H), 2.53–2.80 (m, 2 H), 3.80–4.00 (m, 2 H), and 3.97 (s, 2 H). **1-(2-Diazo-1,3-dioxobutyl)hexahydro-2*H*-azepin-2-one (20)**: yellow crystals; mp 55–56 °C; 95% yield; IR ($CHCl_3$) 2950, 2150, 1690, 1670, 1365, 1325, 1180, 1150,

(36) Sato, M.; Kanuma, N.; Kato, T. *Chem. Pharm. Bull.* **1982**, *30*, 1315.

and 975 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.70–2.05 (m, 6 H), 2.49 (s, 3 H), 2.55–2.80 (m, 2 H), and 3.70–3.95 (m, 2 H).

***N*-Acetyl-*N*-methyl-3-oxobutanamide (28a)**: yellow oil, 51% yield; IR (neat) 3010, 2960, 1740, 1720, 1685, 1415, 1370, 1305, 1140, and 1005 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.22 (s, 3 H), 2.30 (s, 3 H), 3.28 (s, 3 H), and 3.95 (s, 2 H). ***N*-Acetyl-3-diazo-*N*-methyl-3-oxobutanamide (28)**: yellow oil, 90% yield; IR (neat) 3000, 2965, 2925, 2925, 2305, 2135, 1720, 1670, 1135, 1000, and 960 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.30 (s, 3 H), 2.45 (s, 3 H), and 3.23 (s, 3 H).

***N*-Methyl-*N*-(1-oxopropyl)-3-oxobutanamide (29a)**: yellow oil, 42% yield; IR (neat) 2995, 2935, 1725, 1695, 1295, 1115, and 1065 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.07 (t, 3 H, J = 7.2 Hz), 2.20 (s, 3 H), 2.51 (q, 2 H, J = 7.2 Hz), 3.19 (s, 3 H), and 3.90 (s, 2 H). ***N*-Methyl-2-diazo-*N*-(1-oxopropyl)-3-oxobutanamide (29)**: yellow oil, 91% yield; IR (neat) 2995, 2155, 1715, 1660, 1645, 1465, 1430, 1115, 975, and 750 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.80 (t, 3 H, J = 7.5 Hz), 2.45 (s, 3 H), 2.58 (q, 2 H, J = 7.5 Hz), and 3.23 (s, 3 H).

Reaction of 1-(2-Diazo-1,3-dioxobutyl)-2-pyrrolidinone (17) in the Presence of *N*-Phenylmaleimide. A solution containing 340 mg of **17** and 332 mg of *N*-phenylmaleimide in 15 mL of benzene together with a catalytic amount of $Rh_2(OAc)_4$ was placed in an oil bath preheated to 95 °C. The mixture was allowed to reflux for 25 min, and the solvent was removed under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 and filtered through a pad of Celite, and the solvent was removed under reduced pressure. The residue was subjected to silica gel chromatography with an ethyl acetate–hexane mixture as the eluent to give 4-acetyl-4,9a-epoxy-2,3,3a,4,5,9b-hexahydro-1,3,5-trioxo-2-phenyl-1*H*-pyrrolo[3,4-*g*]indolizine (**22a**) as a 1.2:1 mixture of isomers. The minor fraction (35%) contained a white crystalline solid (mp 182–183 °C) whose structure was assigned on the basis of its spectral data: IR ($CHCl_3$) 3030, 3000, 2960, 1790, 1740, 1720, 1600, 1500, 1385, and 1195 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.21–2.25 (m, 2 H), 2.44–2.62 (m, 2 H), 2.65 (s, 3 H), 2.98–3.10 (m, 1 H), 3.74–3.84 (m, 1 H), 3.80 (d, 1 H, J = 8.5 Hz), 3.86 (d, 1 H, J = 8.5 Hz), and 7.12–7.50 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.4, 27.1, 27.3, 43.8, 48.3, 51.6, 92.1, 102.0, 125.9, 128.6, 128.7, 130.4, 168.5, 170.2, 170.7, and 197.0; HRMS calcd for $C_{18}H_{16}N_2O_5$ 340.1059, found 340.1059. Anal. Calcd for $C_{18}H_{16}N_2O_5$: C, 63.53; H, 4.74; N, 8.23. Found: C, 63.45, H,4.69; N, 8.04.

The major fraction (44%) consisted of a white crystalline solid (mp 186–187 °C) whose structure was assigned on the basis of its spectral data: IR ($CHCl_3$) 3020, 1745, 1720, 1600, 1500, 1385, and 1190 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.18–2.29 (m, 2 H), 2.38–2.48 (m, 1 H), 2.58–2.70 (m, 1 H), 2.60 (s, 3 H), 3.19–3.29 (m, 1 H), 3.55 (d, 1 H, J = 6.7 Hz), 3.68–3.78 (m, 1 H), 3.92 (d, 1 H, J = 6.7 Hz), and 7.19–7.49 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.4, 26.0, 27.4, 43.3, 47.4, 52.3, 92.8, 102.6, 125.6, 128.5, 128.6, 130.4, 169.0, 171.1, 171.3, and 196.0; HRMS calcd for $C_{18}H_{16}N_2O_5$ 340.1059, found 340.1059. Anal. Calcd for $C_{18}H_{16}N_2O_5$: C, 63.53; H, 4.74; N, 8.23. Found: C, 63.37; H, 4.52; N, 8.15.

Cycloaddition Reaction of 1-(2-Diazo-1,3-dioxobutyl)-2-azetidinone (18) in the Presence of *N*-Phenylmaleimide. A solution containing 139 mg of **18** and 146 mg of *N*-phenylmaleimide in 8 mL of benzene together with a catalytic amount of rhodium(II) acetate was placed in an oil bath preheated to 95 °C. The mixture was heated at reflux for 2 h, and the solvent was removed under reduced pressure. The resulting residue was subjected to silica gel chromatography with a 90% methylene chloride–ethyl acetate mixture as the eluent to give 4-acetyl-4,8a-epoxy-2,3,3a,8b-tetrahydro-1,3,5-trioxo-2-phenyl-1*H*-pyrrolo[3,4-*d*]-1-azabicyclo[4.2.0]octane (**22b**) as a white crystalline solid (mp 216–217 °C): IR ($CHCl_3$) 3040, 2980, 1765, 1725, 1605, 1500, 1385, 1285, and 1195 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.62 (s, 3 H), 2.78–2.92 (m, 1 H), 3.12–3.26 (m, 1 H), 3.66 (d, 1 H, J = 8.6 Hz), 3.88 (d, 1 H, J = 8.6 Hz), 3.99–4.09 (m, 1 H), 4.11–4.22 (m, 1 H), and 7.16–7.53 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.2, 26.7, 46.9, 49.6, 49.8, 88.3, 99.0, 125.9, 128.6, 128.7, 130.4, 170.2, 170.3, 174.2, 196.8. Anal. Calcd for $C_{17}H_{14}N_2O_5$: C, 62.57; H, 4.32; N, 8.59. Found: C, 62.30; H, 4.36; N, 8.47.

Reaction of 1-(2-Diazo-1,3-dioxobutyl)-2-piperidinone (19) in the Presence of *N*-Phenylmaleimide. A solution containing 267 mg of **19** and 244 mg of *N*-phenylmaleimide in 15 mL of benzene together with a catalytic amount of $Rh_2(OAc)_4$ was placed in an oil bath preheated to 95 °C. The mixture was heated at reflux for 1 h, and the solvent was removed under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 and filtered through a pad of Celite, and the solvent was removed under reduced pressure. The residue was subjected to silica gel chromatography with an ethyl acetate–hexane mixture as the eluent to give 4-acetyl-4,10a-epoxy-2,3,3a,4,7,8,9,10,10a,10b-decahydro-1,3,5-trioxo-2-phenyl-1*H*-pyrrolo[3,4-*a*]-4*H*-quinolizine (**22c**) as a 16:1 mixture of isomers. The minor fraction (5%) consisted of a white crystalline solid (mp 209–210 °C) whose structure was assigned on the basis of its spectral data: IR ($CHCl_3$) 2970, 2940, 1795, 1730, 1605, 1505, 1410, 1390, 1200, and 1025 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.45–1.70 (m, 1 H), 1.75–1.98 (m, 2 H), 2.00–2.28 (m, 2 H), 2.41–2.55 (m, 1 H), 2.60–2.75 (m, 1 H), 2.78 (s, 3 H), 3.74 (d, 1 H, J = 8.2 Hz), 3.81–3.91 (m, 1 H), 3.84 (d, 1 H, J = 8.2 Hz), and 7.10–7.52 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.6, 22.0, 27.5, 29.0, 39.2, 49.0, 56.1, 89.8, 92.5, 126.0, 128.7, 128.8, 130.3, 165.4, 169.6, 170.2, and 197.1; HRMS calcd for $C_{19}H_{18}N_2O_5$ 354.1216, found 354.1214. Anal. Calcd for $C_{19}H_{18}N_2O_5$: C, 64.40; H, 5.12; N, 7.91. Found: C, 64.25, H, 4.98; N, 7.82.

The major fraction (80%) consisted of a white crystalline solid (mp 209–210 °C) whose structure was assigned on the basis of its spectral data: IR ($CHCl_3$) 2960, 2880, 1725, 1505, 1460, 1450, 1390, 1280, 1200, and 1150 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.50–1.75 (m, 2 H), 1.82–2.18 (m, 3 H), 2.50–2.62 (m, 1 H), 2.62 (s, 3 H), 2.72–2.85 (m, 1 H), 3.52 (d, 1 H, J = 6.9 Hz), 3.71 (d, 1 H, J = 6.9 Hz), 3.88–3.98 (m, 1 H), and 7.18–7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.6, 22.8, 25.1, 27.6, 39.0, 48.5, 50.0, 90.5, 93.9, 125.6, 128.5, 128.6, 130.4, 167.2, 170.7, 170.9, and 195.8; HRMS calcd for $C_{19}H_{18}N_2O_5$ 354.1216, found 354.1212. Anal. Calcd for $C_{19}H_{18}N_2O_5$: C, 64.40; H, 5.12; N, 7.91. Found: C, 64.17; H, 4.83; N, 7.86.

Reaction of 1-(2-Diazo-1,3-dioxobutyl)hexahydro-2*H*-azepin-2-one (20) in the Presence of *N*-Phenylmaleimide. A solution containing 299 mg of **20** and 268 mg of *N*-phenylmaleimide in 14 mL of benzene together with a catalytic amount of $Rh_2(OAc)_4$ was placed in an oil bath preheated to 95 °C. The solution was heated at reflux for 1 h, and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and filtered through a pad of Celite, and the solvent was removed under reduced pressure. The residue was subjected to silica gel chromatography with an ethyl acetate–hexane mixture as the eluent to give 4-acetyl-4,11a-epoxy-1,2,2a,4,5,7,8,9,10,11,11a,-11b-dodecahydro-1,3,5-trioxo-2-phenyl-1*H*-pyrrolo[3,5-*a*]pyrido-[1,2-*a*]azepine (**22d**) as a 1.2:1 mixture of isomers. The minor fraction (34%) consisted of a white crystalline solid (mp 183–184 °C) whose structure was assigned on the basis of its spectral data: IR ($CHCl_3$) 2950, 2870, 1790, 1735, 1505, 1435, 1415, 1385, and 1190 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.21–1.43 (m, 2 H), 1.60–1.88 (m, 2 H), 1.90–2.02 (m, 2 H), 2.42–2.55 (m, 2 H), 1.60–1.77 (m, 1 H), 2.72 (s, 3 H), 3.63 (d, 1 H, J = 8.2 Hz), 3.78 (d, 1 H, J = 8.3 Hz), 3.98–4.08 (m, 1 H), and 7.12–7.50 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.6, 27.4, 29.2, 30.0, 32.0, 40.7, 48.4, 54.7, 90.2, 97.6, 125.9, 128.6, 128.8, 130.3, 165.4, 169.8, 170.2, and 197.3; HRMS calcd for $C_{20}H_{20}N_2O_5$ 368.1372, found 368.1370. Anal. Calcd for $C_{20}H_{20}N_2O_5$: C, 65.21; H, 5.47; N, 7.60. Found: C, 65.15, H, 5.29; N, 7.54.

The major fraction (41%) consisted of a white crystalline solid (mp 200–201 °C) whose structure was assigned on the basis of its spectral data: IR ($CHCl_3$) 3040, 2950, 2870, 1720, 1505, 1405, 1390, and 1200 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.30–1.55 (m, 2 H), 1.62–1.81 (m, 1 H), 1.83–2.02 (m, 3 H), 2.20–2.35 (m, 1 H), 2.41–2.57 (m, 1 H), 2.64 (s, 3 H), 2.77–2.90 (m, 1 H), 3.37 (d, 1 H, J = 6.8 Hz), 3.76 (d, 1 H, J = 6.8 Hz), 3.89–3.99 (m, 1 H), and 7.18–7.50 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.4, 27.6, 29.3, 29.4, 30.5, 39.7, 48.5, 53.7, 90.7, 98.3, 125.6, 128.5, 128.6, 130.4, 166.8, 170.8, 170.9, and 196.1; HRMS calcd for $C_{20}H_{20}N_2O_5$ 368.1372, found 368.1374. Anal. Calcd for $C_{20}H_{20}N_2O_5$: C, 65.21; H, 5.47; N, 7.60. Found: C, 65.07; H, 5.13; N, 7.48.

Rhodium(II) Acetate Catalyzed Reaction of Diazo Imides with DMAD. A solution containing 2 mmol of **17** and 1.1 mmol of dimethyl acetylenedicarboxylate in 10 mL of benzene together with a catalytic quantity of $Rh_2(OAc)_4$ was placed in an oil bath

preheated to 95 °C. The mixture was allowed to reflux for 2.5 h, and then the solvent was removed under reduced pressure. The residue was taken up in CH_2Cl_2 and filtered through a pad of Celite, and the solvent was removed under reduced pressure. The resulting residue was subjected to silica gel chromatography using an ethyl acetate–hexane mixture as the eluent. In this manner the following compounds were obtained.

Dimethyl 2-acetyl-5-(3-((methoxycarbonyl)amino)-propyl)-3,4-furandicarboxylate (25): yellow oil (90%); IR (neat) 3400, 3025, 2960, 2890, 1735, 1730, 1690, 1600, 1555, and 1455 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.85–2.00 (m, 2 H), 2.45 (s, 3 H), 3.07 (t, 2 H, J = 7.4 Hz), 3.15–3.25 (m, 2 H), 3.68 (s, 3 H), 3.82 (s, 3 H), 3.95 (s, 3 H), and 5.00–5.18 (br s, 1 H); HRMS calcd for $C_{15}H_{19}NO_8$ 341.1111, found 341.1109.

Dimethyl 2-acetyl-5-methyl-3,4-furandicarboxylate (30): white crystals; mp 57–58 °C; 82% yield; IR ($CHCl_3$) 3030, 2960, 1720, 1680, 1600, 1550, 1445, 1100, 1050, and 815 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 2.45 (s, 3 H), 2.68 (s, 3 H), 3.87 (s, 3 H), and 3.97 (s, 3 H). Anal. Calcd for $C_{11}H_{12}O_6$: C, 54.99; H, 5.04. Found: C, 54.76, H, 5.01.

Dimethyl 2-acetyl-5-ethyl-3,4-furandicarboxylate (31): colorless needles; mp 76–77 °C; 86% yield; IR ($CHCl_3$) 3040, 3000, 2970, 1735, 1690, 1600, 1560, 1450, and 1270 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.29 (t, 3 H, J = 7.6 Hz), 2.45 (s, 3 H), 3.07 (q, 2 H, J = 7.6 Hz), 3.82 (s, 3 H), H), and 3.95 (s, 3 H). Anal. Calcd for $C_{12}H_{14}O_6$: C, 56.69; H, 5.55. Found: C, 56.58; H, 5.57.

Cycloaddition Reaction of *N*-Acetyl-3-diazo-*N*-methyl-3-oxobutanamide (28) in the Presence of *N*-Phenylmaleimide. A solution containig 205 mg of **28** and 214 mg of *N*-phenylmaleimide in 11 mL of benzene was treated with a catalytic amount of $Rh_2(OAc)_4$ and placed in an oil bath preheated to 95 °C. The mixture was allowed to reflux for 2 h, and the solvent was removed under reduced pressure. The resulting residue was subjected to silica gel chromatography using CH_2Cl_2 as the eluent to give 7-acetyl-4,7-epoxy-2,3,3a,4,5,6,7,7a-octahydro-4,5-dimethyl-1,3,6-trioxo-2-phenyl-1*H*-pyrrolo[3,4-*c*]pyridine (**32**) as a 2.6:1 mixture of isomers. The major isomer (55%) was a white crystalline solid (mp 206–207 °C) whose structure was assigned on the basis of its spectroscopic data: IR ($CHCl_3$) 3030, 2970, 1795, 1730, 1605, 1505, 1435, 1410, 1385, and 1190 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.90 (s, 3 H), 2.68 (s, 3 H), 2.73 (s, 3 H), 3.67 (d, 1 H, J = 8.2 Hz), 3.83 (d, 1 H, J = 8.2 Hz), and 7.14–7.52 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.4, 25.9, 27.4, 48.3, 55.3, 90.4, 94.7, 125.9, 128.7, 128.8, 130.3, 166.0, 169.6, 170.0, and 196.9. Anal. Calcd for $C_{17}H_{16}N_2O_5$: C, 62.19; H, 4.92; N, 8.53. Found: C, 62.08; H, 4.92; N, 8.46.

The minor isomer (21%) was obtained as a white crystalline solid (mp 225–226 °C) whose structure was assigned on the basis of its spectroscopic data: IR ($CHCl_3$) 3030, 2950, 1785, 1715, 1600, 1500, 1405, 1380, 1265, and 1195 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.90 (s, 3 H), 2.65 (s, 3 H), 2.88 (s, 3 H), 3.36 (d, 1 H, J = 6.8 Hz), 3.73 (d, 1 H, J = 6.8 Hz), and 7.19–7.50 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.6, 24.8, 27.6, 48.7, 52.5, 90.8, 95.3, 125.6, 128.6, 128.6, 130.4, 167.8, 170.8, 170.8, and 195.8. Anal. Calcd for $C_{17}H_{16}N_2O_5$: C, 62.19; H, 4.92; N, 8.53. Found: C, 62.12; H, 4.95; N, 8.53.

Cycloaddition Reaction of *N*-Methyl-2-diazo-*N*-(1-oxopropyl)-3-oxobutanamide (29) in the Presence of *N*-Phenylmaleimide. A solution containing 208 mg of **29** and 201 mg of *N*-phenylmaleimide in 11 mL of benzene containing a catalytic amount of $Rh_2(OAc)_4$ was placed in an oil bath preheated to 95 °C. The mixture was heated at reflux for 2 h, and the solvent was removed under reduced pressure. The resulting residue was subjected to silica gel chromatography with a methylene chloride–ethyl acetate mixture as the eluent to give 7-acetyl-4,7-epoxy-4-ethyl-2,3,3a,4,5,6,7,7a-octahydro-5-methyl-1,3,6-trioxo-2-phenyl-1*H*-pyrrolo[3,4-*c*]pyridine (**33**) as a 2:1 mixture of isomers. The first fraction contained the minor isomer (21%) as a white crystalline solid (mp 185–186 °C) whose structure was assigned on the basis of its spectroscopic data: IR ($CHCl_3$) 3000, 2960, 1940, 1795, 1730, 1505, 1385, 1190, and 1150 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.10–1.18 (t, 3 H, J = 7.4 Hz), 2.20–2.40 (m, 2 H), 2.61 (s, 3 H), 2.78 (s, 3 H), 3.71 (d, 1 H, J = 8.3 Hz), 3.79 (d, 1 H, J = 8.3 Hz), and 7.10–7.50 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 6.4, 22.7, 26.2, 27.4, 48.3, 53.4, 90.2, 97.5, 125.9, 128.6, 128.7, 130.3, 166.6, 169.8, 170.1, and 197.0. Anal. Calcd for $C_{18}H_{18}N_2O_5$: C, 63.25; H, 5.31; N, 8.18. Found: C, 63.12; H, 5.33; N, 8.12.

The second fraction contained the major isomer (44%) as a white crystalline solid (mp 218–219 °C) whose structure was assigned on the basis of its spectra data: IR ($CHCl_3$) 3040, 3000, 2960, 1795, 1730, 1605, 1510, 1390, 1200, and 1025 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.11 (t, 3 H, J = 7.4 Hz), 2.10–2.35 (m, 2 H), 2.61 (s, 3 H), 2.83 (s, 3 H), 3.36 (d, 1 H, J = 6.9 Hz), 3.73 (d, 1 H, J = 6.9 Hz), and 7.18–7.50 (m, 5 H). Anal. Calcd for $C_{18}H_{18}N_2O_5$: C: 63.25; H, 5.31; N, 8.18. Found: C, 63.23; H, 5.34; N, 8.16.

Preparation and Rhodium(II) Octanoate Catalyzed Reaction of *N*-(Diazoacetoacetyl)-*N*-phenyl-1-pyrrolidinecarboxamide (40) with DMAD. *N*-Phenyl-1-pyrrolidinecarboxamide was prepared from 2.6 g (3 mL, 36 mmol) of pyrrolidine, 1.7 g (40 mmol) of hexane-washed 60% sodium hydride dispersion in mineral oil, and 4.71 g (40 mmol) of phenyl isocyanate in 230 mL of dry ether according to the general procedure of Kraus and co-workers.[37] The crude solid was recrystallized from dichloromethane–ether to give white needles of the urea in 97% yield: mp 133–134 °C (lit.[38] mp 135–136 °C); IR ($CHCl_3$) 3460, 3010, 2820, 1660, 1600, 1525, 1445, 1375, 1245, and 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.94–1.98 (m, 4 H, J = 6.6 Hz), 3.43–3.47 (t, 4 H, J = 6.6 Hz), 6.12 (br s, 1 H), and 6.97–7.41 (m, 5 H). Anal. Calcd for $C_{11}H_{14}N_2O$: C, 69.43; H, 7.42; N, 14.73. Found: C, 69.28; H, 7.40; N, 14.69.

A solution containing 1.50 g (7.9 mmol) of the above compound in 20 mL of dry tetrahydrofuran was cooled to −78 °C under a nitrogen atmosphere. To this solution was added 6.1 mL of a 1.4 M *n*-butyllithium solution in hexane followed by a solution of 0.7 mL in diketene (8.7 mmol) in 3 mL of dry tetrahydrofuran according to the general procedure of Doyle.[39] Purification by radial chromatography was carried out using an ethyl acetate–hexane mixture as the eluent. In addition to recovered starting material, *N*-acetoacetyl-*N*-phenyl-1-pyrrolidinecarboxamide (42% yield) was obtained as a pale yellow oil: IR ($CHCl_3$) 1720 and 1675 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.81–1.85 (m, 4 H), 2.18 (s, 3 H), 3.20–3.52 (m, 4 H), 3.72 (s, 2 H), and 7.22–7.40 (m, 5 H); HRMS calcd for $C_{15}H_{18}N_2O_3$ 274.1317, found 274.1309.

To a solution containing 790 mg of the above material and 100 mg (0.8 mmol) of mesyl azide in 1 mL of acetonitrile at 25 °C was added 110 mg (1.1 mmol) of triethylamine. The reaction was stirred for 26 h at 25 °C and worked up according to the general method of Taber.[40] Purification was carred out by radial chromatography with a 20% ethyl acetate–hexane mixture as the eluent to give *N*-(diazoacetoacetyl)-*N*-phenyl-1-pyrrolidinecarboxamide (**40**) (90% yield): IR ($CHCl_3$) 3010, 2820, 2130, 1660, 1595, 1425, and 1375 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.78–1.82 (m, 4 H), 2.36 (s, 3 H), 3.35–3.40 (m, 4 H), and 7.12–7.39 (m, 5 H).

To a solution containing 196 mg of the above compound and 1 equiv of DMAD in 4 mL of dry benzene at 25 °C was added a catalytic amount of rhodium(II) octanoate. The reaction mixture was stirred at 25 °C for 15 min and was then concentrated under reduced pressure to give dimethyl 2-acetyl-5-pyrrolidine-3,4-furandicarboxylate (**41**) in 100% yield. The crude residue was purified by silica gel radial chromatography with a hexane–ether mixture as the eluent. Recrystallization of the major fraction from ether–dichloromethane afforded white needles of furan **41**: mp 160–161 °C; IR ($CHCl_3$) 3000, 2950, 2880, 1740, 1705, 1655, 1645, 1590, 1570, 1455, 1370, 1334, 1240, 1140, 1100, 1060, 730, and 670 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.92–1.97 (m, 4 H), 2.27 (s, 3 H), 3.66–3.70 (m, 4 H), 3.68 (s, 3 H), and 3.90 (s, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 25.4, 25.7, 49.9, 51.4, 52.9, 91.5, 128.6, 138.4, 159.0, 162.2, 164.7, 183.8. Anal. Calcd for $C_{14}H_{17}NO_6$: C, 56.93; H, 5.81; N, 4.75. Found: C, 56.78; H, 5.79; N, 4.72.

Preparation and Rhodium(II) Octanoate Catalyzed Reaction of *N'*-(Diazoacetoacetyl)-*N'*-phenyl-*N*,*N*-bis(phenylmethyl)urea (45) with Dimethyl Acetylenedicarboxylate.

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N'-Phenyl-*N,N*-bis(phenylmethyl)urea was prepared from 500 mg (2.5 mmol) of dibenzylamine, 70 mg (2.75 mmol) of sodium hydroxide, and 330 mg (2.75 mmol) of phenyl isocyanate in 16 mL of dry DMF according to the general procedure of Kraus and co-workers.[37] The resulting solid was recrystallized from ether, affording the urea in 98% yield as a white solid: mp 116–117 °C (lit.[41] mp 123–124 °C), IR (KBr) 3480, 3260, 3060, 2920, 1640, 1600, 1540, 1490, 1440, 1310, 1230, 775, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 4.60 (s, 4 H), 6.29 (s, 1 H), and 7.18–7.42 (m, 15 H). Anal. Calcd for $C_{21}H_{20}N_2O$: C, 79.71; H, 6.38; N, 8.86. Found: C, 79.78; H, 6.39; N, 8.81.

A solution containing 550 mg (1.8 mmol) of the above urea in 4 mL of anhydrous tetrahydrofuran was cooled to −78 °C under a nitrogen atmosphere. To this solution was added 1.5 mL of a 1.4 M *n*-butyllithium solution in hexane followed by a solution containing 170 mg of diketene (2 mmol) in 1 mL of THF according to the general procedure of Doyle.[39] Purification of the residue by radial chromatography with a 2:3 hexane–ether mixture as the eluent afforded 269 mg (38% yield) of *N'*-acetoacetyl-*N'*-phenyl-*N,N*-bis(phenylmethyl)urea as a yellow oil: IR (neat) 3080, 3040, 2940, 1730, 1700, 1630, 1595, 1500, 1460, 1420, 1160, 1080, 1030, 750, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.09 (s, 3 H), 3.53 (s, 2 H), 4.53 (s, 4 H), and 7.26–7.38 (m, 15 H); HRMS calcd for $C_{25}H_{24}N_2O_3$ 400.1786, found 400.1782.

To a solution containing 150 mg (0.38 mmol) of the above compound and 83 mg (0.42 mmol) of mesyl azide in 0.75 mL of CH_3CN at 25 °C was added 77 mg (0.76 mmol) of Et_3N. The reaction mixture was stirred overnight and worked up according to the general method of Taber.[40] Purification by radial chromatography with a 2:3 hexane–ether mixture as the eluent afforded 119 mg (75% yield) of *N'*-(diazoacetoacetyl)-*N'*-phenyl-*N,N*-bis(phenylmethyl)urea (**45**) as a bright yellow solid: mp 49–50 °C; IR ($CHCl_3$) 3000, 2130, 1690, 1680, 1630, 1330, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.48 (s, 3 H), 4.49 (s, 4 H), and 7.07–7.35 (m, 15 H); HRMS calcd for $C_{25}H_{22}N_2O_3$ ($M^+ - N_2$) 398.1630, found 398.1627.

To a solution containing 92 mg (0.22 mmol) of (diazoacetoacetyl)urea **45** and 40 mg (0.28 mmol) of distilled DMAD in 3 mL of dry benzene at 25 °C was added a catalytic quantity of rhodium(II) octanoate. Gas evolution was observed for approximately 40 min. The reaction mixture was stirred for an additional 2 h and then concentrated under reduced pressure to give 4-acetyl-5,6-dicarbomethoxy-1-(dibenzylamino)-7-oxa-3-oxo-2-phenyl-2-azabicyclo[2.2.1]hept-5-ene (**46**) in 47% yield. The crude residue was purified by silica gel radial chromatography with a 2:3 hexane–ether mixture as the eluent to give a pure sample of cycloadduct **46** as a pale yellow oil: IR ($CHCl_3$) 3015, 2960, 1750, 1715, 1675, 1570, 1460, 1370, and 1240 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.25 (s, 3 H), 3.69 (s, 3 H), 3.93 (s, 3 H), 4.73 (s, 4 H), and 7.21–7.35 (m, 15 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 25.9, 51.8, 53.0, 53.4, 77.2, 93.9, 120.1, 123.4, 127.8, 127.9, 128.0, 128.8, 129.0, 135.9, 138.7, 160.5, 162.1, 164.6, and 184.4; *m/e* (M + H) 541; HRMS calcd for $C_{24}H_{23}NO_6$ (M^+ – PhNCO) 421.1525, found 421.1529.

Rhodium(II) Octanoate Catalyzed Reaction of *N'*-(Diazoacetoacetyl)-*N'*-phenyl-*N,N*-bis(phenylmethyl)urea (45) with Methyl Propiolate. To a solution containing 97 mg (0.23 mmol) of (diazoacetoacetyl)urea **45** and 25 mg (0.29 mmol) of methyl propiolate in 3 mL of dry benzene at 25 °C was added a catalytic quantity of rhodium(II) octanoate under N_2. The reaction mixture was stirred for 4.5 h, and then the solvent was removed under reduced pressure to give a 2:1 mixture of 4-acetyl-6-carbomethoxy-1-(dibenzylamino)-5*H*-7-oxa-3-oxo-2-phenyl-2-azabicyclo[2.2.1]hept-5-ene (**47**) (50%) and 4-acetyl-5-carbmethoxy-1-(dibenzylamino)-6*H*-7-oxa-3-oxo-2-phenyl-2-azabicyclo[2.2.1]hept-5-ene (**48**) (25%). The crude residue was purified by radial chromatography with a 2:3 hexane–ether mixture. The first fraction isolated corresponded to cycloadduct **47** as a pale yellow oil; IR ($CHCl_3$) 3100, 3070, 3005, 2960, 1710, 1655, 1595, 1560, 1455, 1170, 1105, and 710 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.31 (s, 3 H), 3.73 (s, 3 H), 4.81 (s, 4 H), 7.21–7.34 (m, 15 H), and 7.51 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.0, 51.5, 52.7, 77.2, 94.2, 124.4, 124.4, 127.7, 128.0, 128.2, 128.4, 128.7, 129.0, 136.3, 141.6, 162.0, 163.2, and 183.4; HRMS calcd for $C_{22}H_{21}NO_4$ (M^+ – PhNCO) 363.1470, found 363.1474.

The second fraction contained cycloadduct **48** as a pale yellow oil: IR ($CHCl_3$) 3095, 3070, 3000, 2950, 1730, 1680, 1585, 1535, 1405, 1170, 1115, and 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.32 (s, 3 H), 3.83 (s, 3 H), 4.37 (s, 4 H), 6.99–7.29 (m, 15 H), and 7.40 (s, 1 H); HRMS calcd for $C_{22}H_{21}NO_4$ (M^+ – PhNCO) 363.1470, found 363.1463.

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Registry No. **3**, 126556-94-3; **4**, 130935-20-5; **5**, 126556-96-5; **6**, 126556-97-6; **7**, 126556-98-7; **8**, 126556-99-8; **10**, 130935-21-6; **11**, 130935-22-7; **12**, 130935-23-8; **13**, 126557-00-4; **14**, 126557-02-6; **15**, 126557-01-5; **16**, 126557-03-7; **17**, 126685-93-6; **17a**, 53544-25-5; **18**, 126685-94-7; **18a**, 126686-09-7; **19**, 126685-95-8; **19a**, 33720-94-4; **20**, 126685-96-9; **20a**, 14826-58-5; **22a** (isomer 1), 130935-24-9; **22a** (isomer 2), 130982-87-5; **22b**, 126686-06-4; **22c** (isomer 1), 130982-88-6; **22c** (isomer 2), 130982-89-7; **22d** (isomer 1), 126686-08-6; **22d** (isomer 2), 126784-70-1; **25**, 126685-97-0; **28**, 126685-99-2; **28a**, 61334-44-9; **29**, 126686-00-8; **29a**, 130935-25-0; **30**, 31536-91-1; **31**, 126686-01-9; **32** (isomer 1), 130935-26-1; **32** (isomer 2), 130982-90-0; **33** (isomer 1), 130935-27-2; **33** (isomer 2), 130982-91-1; **40**, 130935-28-3; **41**, 130935-29-4; **45**, 130935-30-7; **46**, 130935-31-8; **47**, 130935-32-9; **48**, 130935-33-0; *t*-BuNH-$(CH_2)_2$COOEt, 1462-98-2; EtOCO$(CH_2)_2$NHCH$_2$C$(CH_3)_3$, 130935-34-1; *t*-BuOCO$(CH_2)_2$NHCH$_2$C$(CH_3)_3$, 130935-35-2; BuNH$(CH_2)_2$COOEt, 10494-81-2; $Rh_2(OAc)_4$, 15956-28-2; Rh_2-$(pfb)_4$, 73755-28-9; MeCONHMe, 79-16-3; $H_3CCH_2CONHMe$, 1187-58-2; diketene, 674-82-8; 2,2,6-trimethyl-1,3-dioxen-4-one, 5394-63-8; 2-azetidinone, 930-21-2; 2-pyrrolidinone, 616-45-5; 2-piperidinone, 675-20-7; hexahydro-1*H*-azepine-2-one, 105-60-2; *N*-phenylmaleimide, 941-69-5; rhodium(II) octanoate, 68803-87-2; pyrrolidine, 123-75-1; phenyl isocyanate, 103-71-9; *N*-phenyl-1-pyrrolidinecarboxamide, 5626-53-9; *N*-acetoacetyl-*N*-phenyl-1-pyrrolidinecarboxamide, 130935-36-3; dibenzylamine, 103-49-1; urea, 57-13-6; *N'*-acetoacetyl-*N'*-phnyl-*N,N*-bis(phenylmethyl)-urea, 130935-37-4; methyl propiolate, 922-67-8.

Supplementary Material Available: ^1H NMR and ^{13}C NMR spectra (75 MHz) for all compounds with high-resolution mass spectra (38 pages). Ordering information is given on any current masthead page.

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