7.35 (m, 5 H); NMR **33** δ 1.22 (t, 3 H, J = 7.1 Hz), 2.54 (d, 4 H, J = 7.3 Hz), 2.80 (s, 3 H), 4.12 (q, 2 H, J = 7.1 Hz), 4.58 (br s, 1 H), 4.84 (d, 1 H, J = 2.5 Hz), 5.00–5.10 (m, 4 H), 5.55–5.70 (m, 2 H), and 7.20 (m, 5 H).

To a solution containing 0.57 mmol of LDA in 30 mL of tetrahydrofuran at −78 °C under a nitrogen atmosphere was added 0.14 g of **27** via syringe. The resulting orange solution was stirred at −78 °C for 10 min, and then 0.31 g of HMPA was slowly added via syringe. The solution was stirred for an additional 30 min, and then 0.12 g of benzaldehyde was added. After stirring for 30 min at −78 °C, the solution was allowed to warm to room temperature and was quenched with a saturated ammonium chloride solution. The solvent was removed under reduced pressure, and the residue was taken up in methylene chloride. The organic layer was washed with a saturated ammonium chloride solution followed by water to remove the HMPA. The solution was then dried over magnesium sulfate and concentrated under reduced pressure to give a yellow oil. This material was chromatographed on a silica gel column with use of a 20% ethyl acetate–hexane mixture as the eluent. The major fraction contained 0.10 g (57% yield) of a yellow oil whose structure was assigned as carboxylic acid **35** on the basis of its spectral properties: IR (CCl_4) 3000 (br), 2600 (br), 1670, 1590, 1490, 1440, 1415, 1345, 1250, 1195, 1170, 1080, and 1060 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 2.78 (s, 3 H), 4.95 (s, 1 H), 5.55 (s, 1 H), 7.20–7.45 (m, 11 H), and 8.82 (s, 1 H); HRMS calcd for $C_{19}H_{17}NO_3$ 307.1208, found 307.1198. On one occasion an intermediate lactone was isolated whose structure was assigned as **34** on the basis of its NMR spectrum: NMR ($CDCl_3$, 300 MHz) δ 2.82 (s, 3 H), 3.62 (d, 1 H, J = 11.3 Hz), 3.95 (t, 1 H, J = 11.3 Hz), 5.24 (d, 1 H, J = 11.3 Hz), 5.28 (s, 1 H), and 6.95–7.15 (m, 10 H).

Zinc-Induced Reduction of *N*-Methyl-3-phenyl-5-(carbethoxymethylene)isoxazolidine (27). A solution containing 200 mg of **27** and 510 mg of activated zinc dust in 10 mL of a 50% aqueous acetic acid solution was stirred at room temperature for 36 h. The solution was filtered, and the filtrate was neutralized with sodium bicarbonate. The solution was extracted with methylene chloride, and the combined extracts were washed with water, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure to leave behind a yellow oil. This material was chromatographed on a silica gel column with a 20% ethyl acetate–hexane mixture as the eluent. The major fraction contained 0.11 g (62% yield) of a clear oil whose structure was assigned as ethyl 3-oxo-5-phenylpent-4-enoate (**39**) as a mixture of the keto and enol tautomers on the basis of its spectral properties: IR (neat) 3000, 1745, 1650, and 1605 cm^{-1}; NMR ($CDCl_3$, 300 MHz) keto tautomer δ 1.30 (t, 3 H, J = 7.1 Hz), 3.70 (s, 2 H), 4.22 (q, 2 H, J = 7.1 Hz), 6.42 (d, 1 H, J = 16.0 Hz), 6.80 (d, 1 H, J = 16.0 Hz), and 7.30–7.60 (m, 5 H); enol tautomer δ 1.27 (t, 3 H, J = 7.1 Hz), 4.20 (q, 2 H, J = 7.1 Hz), 5.15 (s, 1 H), 7.30–7.60 (m, 7 H), and 12.00 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.1, 14.2, 47.6, 60.1, 61.3, 91.8, 121.8, 125.2, 127.5, 128.4, 128.7, 128.9, 129.2, 130.8, 134.1, 135.3, 136.7, 144.5, 167.3, 169.1, 172.7, and 191.8; HMRS calcd for $C_{13}H_{14}O_3$ 218.0943, found 218.0947.

A solution containing 0.50 g of **27** and 1.57 g of activated zinc dust in 20 mL of a 50% aqueous acetic acid solution was stirred at 80 °C for 16 h and allowed to cool to room temperature. The solution was filtered, and the filtrate was neutralized with sodium bicarbonate. The solution was extracted with methylene chloride, and the combined extracts were washed with water, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure to leave behind a yellow oil. This material was chromatographed on a silica gel column with use of a 20% ethyl acetate–hexane mixture as the eluent. The major fraction contained 0.13 g (30% yield) of a clear oil whose structure was assigned as ethyl 3-oxo-5-phenylpentanoate (**40**) on the basis of its spectral properties: IR (neat) 3030, 2990, 2940, 1745, 1715, 1650, 1500, 1455, 1375, 1320, 1260, 1190, 1165, and 1035 cm^{-1}; NMR ($CDCl_3$, 300 MHz) keto tautomer δ 1.15 (t, 3 H, J = 7.1 Hz), 2.80 (m, 4 H), 3.35 (s, 2 H), 4.05 (q, 2 H, J = 7.1 Hz), and 7.10–7.30 (m, 5 H); HRMS calcd for $C_{13}H_{16}O_3$ 220.1099, found 220.1095.

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health. Use of the high-field NMR spectrometer used in these studies was made possible through a NSF equipment grant.

Registry No. **4**, 118171-16-7; **5**, 118171-17-8; **6**, 107081-91-4; **7**, 118171-18-9; **8**, 118171-19-0; **9**, 21422-40-2; **15**, 2525-55-5; **16**, 118171-20-3; **17**, 118171-21-4; **19** isomer 1, 118171-22-5; **19** isomer 2, 118171-37-2; **20**, 118171-23-6; **21**, 118171-24-7; **22**, 117620-34-5; **24**, 117620-35-6; **25**, 118171-25-8; **26**, 118171-26-9; **27**, 118171-27-0; **28**, 118171-28-1; **29** isomer 1, 118171-29-2; **29** isomer 2, 118171-36-1; **30**, 118171-30-5; **31**, 118171-31-6; **32**, 118171-32-7; **33**, 118171-33-8; **34**, 118171-34-9; **35**, 118171-35-0; **39**, 1503-99-7; **40**, 17071-29-3; *C,N*-diphenylnitrone, 1137-96-8; (phenylsulfonyl)propadiene, 2525-42-0; methyl 2,3-butadienoate, 18913-35-4; *N*-methyl-*C*-phenylnitrone, 3376-23-6; *N*-phenylhydroxylamine, 100-65-2; ethyl 2,3-butadienoate, 14369-81-4; sodium benzenesulfonate, 515-42-4; *N*-hydroxypiperidine, 4801-58-5.

Supplementary Material Available: The final positions and thermal parameters of the X-ray analysis of benzazepinone **5** are given in Tables 1–5 (4 pages). Ordering information is given on any current masthead page.

Reactivity Patterns in the Rhodium Carbenoid Induced Tandem Cyclization–Cycloaddition Reaction

Albert Padwa,* Susan F. Hornbuckle, Glen E. Fryxell, and Paul D. Stull

Department of Chemistry, Emory University, Atlanta, Georgia 30322

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The rhodium(II) acetate catalyzed behavior of *o*-[(propenyloxy)methyl]-α-diazoacetophenone was studied. The results obtained are consistent with a mechanism in which the key step involves intramolecular cyclization of the ketocarbenoid onto the oxygen atom of the side chain to give an oxonium ylide intermediate which undergoes either C–H insertion or a competitive 2,3-sigmatropic rearrangement. The reaction of 1-diazo-9-decene-2,5-dione with rhodium(II) acetate results in cyclization of the intermediate rhodium carbenoid to give a six-ring carbonyl ylide which readily undergoes intramolecular dipolar cycloaddition. This reaction does not occur when the keto group of the diazo compound has been replaced by an ester functionality. Similar results were also obtained with *cis*-2-benzoyl-1-(diazoacetyl)cyclopentane.

The stereoselective preparation of highly substituted oxygen heterocycles, especially structurally complex tetrahydrofurans and tetrahydropyrans, has attracted considerable attention and provides a challenging synthetic

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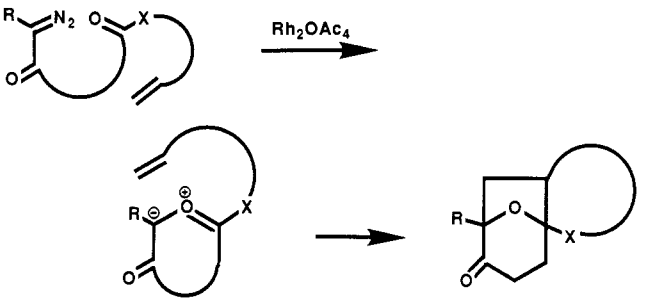
problem.[1-10] Over the past decade there has been a growing interest in the use of carbonyl ylides as 1,3-dipoles for the total synthesis of oxygenated heterocycles.[11-20] The development of methodology using these oxygen-based reactive intermediates, however, has lagged far behind those based on other 1,3-dipoles.[21] One of the simplest routes for the generation of carbonyl ylides involves the addition of a carbene onto the oxygen atom of a carbonyl group.[22-31] The intramolecular reaction of carbenes with carbonyl groups results in the formation of cyclic carbonyl ylides. This approach, pioneered largely by Ibata and co-workers,[27] allows for the convenient generation of various five- or six-membered carbonyl ylides which can be trapped by π-bonds. Generation of the carbene center involves treating a diazo compound with an appropriate transition-metal catalyst.[32,33] The preferred catalyst for executing this transformation is rhodium(II) acetate dimer.[34,35]

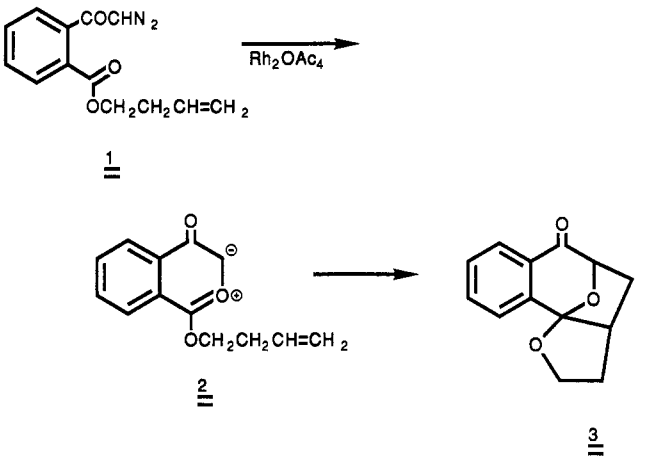
Our work in this area has been focused on those cases in which the diazo functionality, the trapping carbonyl group, and the π-bond are in the same molecule.[36] The resulting cycloadduct contains three new rings that have



been assembled in one step in a highly stereospecific manner.[37] Our ongoing interest in the generality and synthetic utility of this method inspired us to take a detailed look at the scope and mechanistic details of this process. During the course of our studies, certain unanticipated results were obtained, which we now wish to report.

Results and Discussion

Our initial forays into this tandem cyclization–cycloaddition chemistry involved systems in which the keto rhodium carbenoid and the remote carbonyl were attached in a 1,2-fashion on a benzene ring.[36] The early success with the ortho-substituted diazoacetophenone system 1 suggested to us that constraining the geometry of the carbenoid center relative to the remote carbonyl should be beneficial to dipole formation. To this end we investigated the rhodium(II)-catalyzed reaction of diazo keto esters 4 and 5.



It should be noted that the previous substrates studied have been diazoacetophenone derivatives while these

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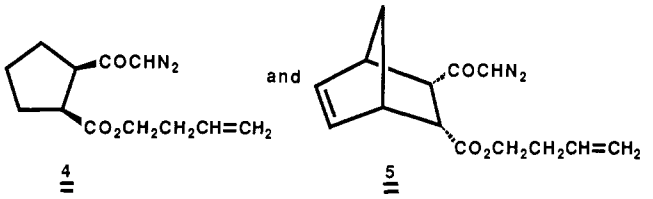
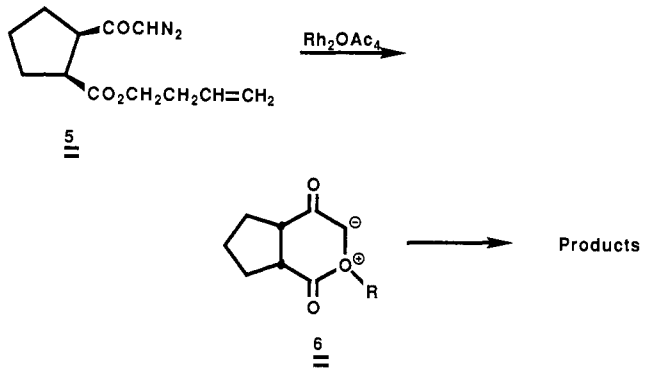
compounds are aliphatic diazo keto esters. Nevertheless, the same number of carbon atoms separates the diazo ketone moiety from the carbalkoxy functionality, and the only difference is the dissimilarity in hybridization. With these points in mind, compound **4** (or **5**) was dissolved in



4 5

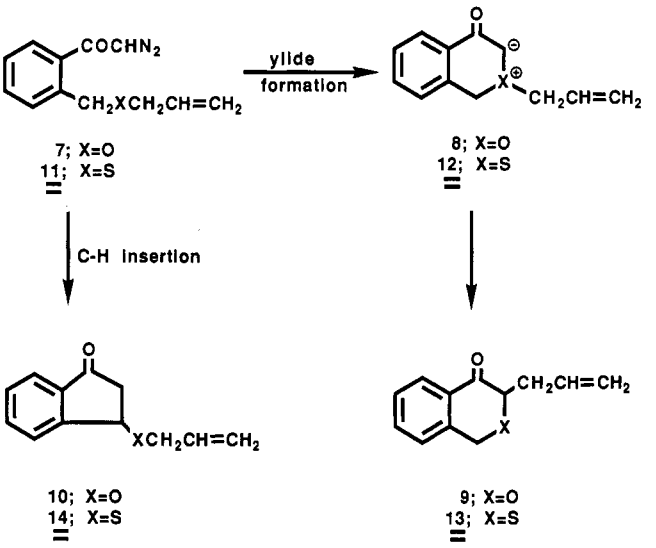
benzene, $Rh_2(OAc)_4$ was added, and the reaction mixture was placed in an oil bath preheated to 80–90 °C. Although the starting material was consumed, no intramolecular dipolar cycloadduct was detected in the crude reaction mixture. Since we were unable to identify any of the products, it is impossible to say whether carbonyl ylide formation did occur or whether the reaction took an entirely different course. Interestingly, no bimolecular dipolar cycloadduct could be obtained when the rhodium-catalyzed reaction was carried out in the presence of dimethyl acetylenedicarboxylate. This result is strikingly different from that encountered in the diazoacetophenone series wherein bimolecular cycloadducts could be isolated in good yield.

The difference in reactivity between the two systems could be due to conformational factors wherein the carbonyl and rhodium carbenoid centers present in **5** were being held apart by their rigid aliphatic backbones. Instead of the ester carbonyl group attacking the rhodium carbenoid, the reaction could occur from intermediate **6**, which is derived by attack of the *O*-ester oxygen atom with the electron-deficient carbenoid center. In order to probe this possibility, we decided to study the chemistry of a number of simpler systems.



5 6

Ylide formation as a result of carbene interaction with the unshared electron pair of heteroatoms has been extensively studied.[38] In contrast to the abundant literature on nitrogen, phosphorus, and sulfur,[38,39] little was known about oxygen ylides[40–42] when we started our work in this area. It occurred to us that oxonium ylides of type **8** should be readily formed by treating 2-diazo-1-[2-[(2-propenyloxy)methyl]phenyl]ethanone (**7**) with rhodium(II) acetate. Earlier studies in the literature have shown that the metal-catalyzed reactions of diazo compound with a broad selection of allylic substrates result in products derived from 2,3-sigmatropic rearrangement of intermediate allylic ylides.[42] We have found that a related process occurs upon treating **7** with rhodium(II) acetate in benzene at room temperature. In this case a mixture of two compounds



was formed and the substrates were identified as 3-allyl-2-isochroman-4-one (**9**) (43%) and 2,3-dihydro-3-(2-propenyloxy)-1*H*-inden-1-one (**10**) (35%). Structure **9** is consistent with carbenoid generation followed by capture by the neighboring oxygen atom to generate oxonium ylide **8**, which undergoes a subsequent 2,3-sigmatropic rearrangement. While our work was in progress, independent reports by Pirrung[43] and Johnson[44] appeared, describing analogous processes.

Indenone **10** is formed by a competitive C–H insertion reaction which occurs between the metal-stabilized carbene and the benzylic hydrogens. There are a variety of examples in the literature of intramolecular C–H insertion by diazo ketones,[45] thereby providing a good precedent for the formation of **10**. Results obtained by Taber and Petty[46] show that there is a kinetic preference for five membered ring formation, although C–H insertion giving other size rings is also possible. The regioselectivity one obtains in a particular molecule depends upon the type of diazo function, substitution of the carbon where insertion takes place, steric factors, and the reagent used to promote the reaction. The isolation of indenone **10** establishes that benzylic C–H insertion is substantially more rapid than allylic C–H insertion with this particular system.

The above results clearly establish that C–H insertion of the rhodium carbenoid can be competitive with ylide formation and 2,3-sigmatropic rearrangement. In order to assess the importance of the heteroatom to the product distribution, we studied the rhodium-catalyzed reaction of the closely related thio-substituted diazo ketone **11**. Treatment of **11** with rhodium(II) acetate resulted in the formation of both **13** and **14**. In this case, however, the ratio of ylide formation to C–H insertion (i.e., **13**:**14**) was 9:1, in marked contrast to the 1.2:1 ratio obtained from **7**. This would suggest that the larger and more polarizable sulfur atom is much more effective in coordination with

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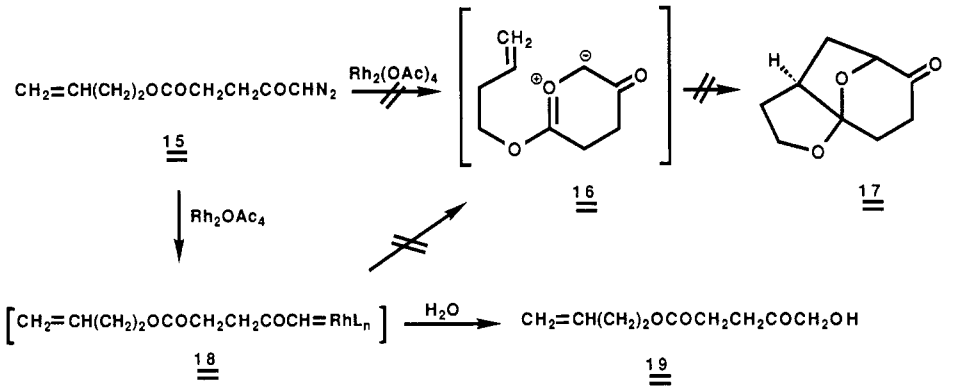
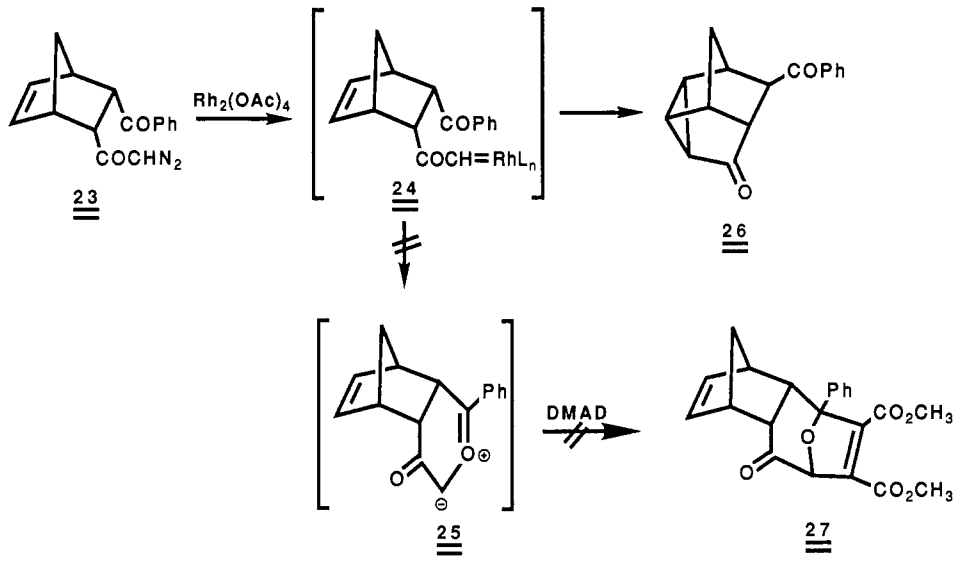
Scheme I



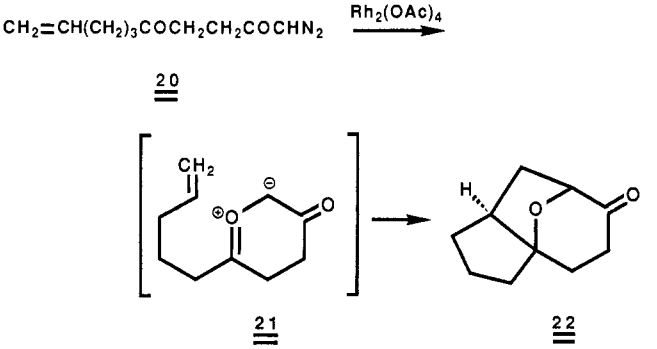
Scheme II



the metal carbene center. The product distribution is also consistent with the relative nucleophilicities of the two heteroatoms.[47]

The question of whether oxonium ylide formation is involved in the chemistry of diazo keto esters **4** and **5** remains unanswered since we were unable to isolate any characterizable products from these systems. This led us to study the rhodium(II)-catalyzed behavior of the conformationally unencumbered diazo keto ester **15** (Scheme I). Treatment of **15** with a catalytic amount of rhodium(II) acetate dimer in benzene led to the formation of hydroxymethyl ketone **19** (53%) together with a complex mixture of products, none of which appeared to arise via cycloaddition of the desired carbonyl ylide **16**.[48] A wide variety of catalysts and conditions were employed with diazo keto ester **15**, and in no case was any evidence for cycloadduct **17** found.[49] Moreover, the isolation of hydroxymethyl ketone **19** as the major product would tend to eliminate the involvement of a cyclic oxonium ylide with this system.

Extension of the carbenoid insertion methodology to the closely analogous keto system **20** was next investigated. In striking contrast to the results obtained with diazo keto ester **15**, the reaction of **20** with Rh_2OAc_4 proceeded quite smoothly, producing cycloadduct **22** in 75% yield. Interestingly, no bimolecular trapping product was observed when the reaction of **20** was carried out with rhodium(II) acetate in the presence of dimethyl acetylenedicarboxylate. With this system, intramolecular cycloaddition to the internal π-bond is too rapid to allow bimolecular trapping of the intermediate carbonyl ylide (i.e., **21**).



The results encountered with the above two systems suggest that the electronic difference between an ester and a ketone carbonyl group creates alternate competing

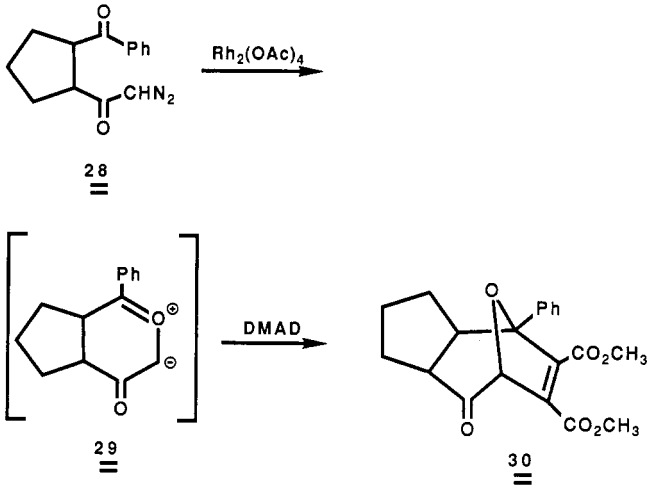
(47) The effectiveness of sulfur as a trap for electrophilic carbenes has been known for a long time, and intermolecular reactions of allyl sulfides and allyl ethers have been used to compare the relative effectiveness of sulfur.[39] What is surprising is not just the increase in the 13:14 ratio when X = S but the fact that **14** is seen at all in this case.

(48) An alternate possibility suggested by a referee is that carbonyl ylide **16** may have been formed but is sufficiently stable to only react with water to give **19**. It should be noted, however, that carbonyl ylide dipoles have never been isolated as a consequence of their high reactivity. All of our attempts to detect an intermediate dipole in this system were unsuccessful.

(49) The following catalysts and conditions were examined: ($Rh_2OAc)_4$, $Rh_2(OAc)_4$·pyridine; $RH_2(OAc)_4$·pyridine; $Rh_2(PFB)_4$; $Rh_6(CO)_{16}$; Rh/C; Rh/Al_2O_3; $Cu(OTF)_2$; $Cu(acac)_2$; Cu powder; $Pd(OAc)_2$; $PdCl_2$; $Pd(PhCN)_2Cl_2$; $h\nu$, xylene reflux; $Ag(OAc)$; $Mo(CO)_6/h\nu$; $Cr(CO)_6/h\nu$; $W(CO)_6/h\nu$; $Fe_2(CO)_9/h\nu$; BF_3·OEt_2; $MgBr_2$·OEt_2.

pathways in these aliphatic systems. In order to provide additional clarification of this point, we felt that a comparison of the rhodium(II)-catalyzed behavior of the ketonic analogues of diazo keto esters **4** and **5** would be enlightening. When diazo ketone **23** was stirred in benzene with 2 mol % of $Rh_2(OAc)_4$ and a slight excess of DMAD, cyclopropane **26** was formed in 74% yield as the only identifiable product (Scheme II). Compound **26** is clearly arising via intramolecular carbenoid addition across the carbon–carbon double bond[45] followed by a subsequent endo-exo isomerization about the benzoyl group.[50] Thus, the preference for the rhodium carbenoid to undergo internal cycloaddition completely overwhelms any tendency for carbonyl ylide formation.[51]

We have also examined the rhodium acetate induced behavior of the keto analogue of diazo ester **4**. When *cis*-1-(diazoacetyl)-2-benzoylcyclopentane (**28**) was exposed to the usual reaction conditions, cycloadduct **30** was formed cleanly and in high yield. This result clearly establishes



that the inefficiency of carbonyl ylide formation observed with diazo keto ester **4** is due to electronic differences in the trapping carbonyl group and is not related to any conformational constaints imposed by the cyclic backbone. It should be emphasized that this ester/ketone dichotomy has surfaced only in those systems in which the carbenoid and carbonyl groups are connected with an aliphatic tether. In those cases in which the reacting centers are connected in a 1,2-fashion on a benzene ring (i.e., **1**), dipole formation and cycloaddition proceed smoothly. This may be due to the fact that, in the benzo systems, ring closure of the rhodium carbenoid affords an aromatic dipole.

So the major unanswered mechanistic question is: why does the replacement of the keto group on the side chain with an ester functionality, a seemingly innocuous transformation, completely change the path of reaction? The catalytic activity of transition-metal compounds depends on the coordination unsaturation at the metal center which allows reaction with diazo compounds as electrophiles.[33] Addition to the diazo compound is believed to cause the loss of nitrogen and production of an electrophilic metal-stabilized carbene.[38] Lewis bases may compete with the diazo compound for the available coordination site on the electrophilic transition metal, but so long as this inhibition is reversible, the chemical outcome of the transformation is not altered. Rhodium(II) acetate corresponds to a binuclear rhodium compound with one available coordination site per metal center and is an exceptionally effective catalyst for a wide variety of catalytic transformations involving diazo compounds.[34,35] Rhodium(II) acetate is not susceptible to redox transformations with diazo compounds and does not form π-complexes with olefins. The discrepancy between the diazo keto ester's reactivity and that of the diazo dione analogue remains an unanswered question for the moment.

In conclusion, two general trends have surfaced from our studies in this area. First and foremost, trapping of a rhodium carbenoid with a ketonic carbonyl group is a useful method for the preparation and subsequent cycloaddition of carbonyl ylides. This approach can be used for both inter- and intramolecular cycloadditions. Secondly, in those cases where the trapping carbonyl is an ester, alternate reaction pathways may compete with dipole formation. In aromatic systems this competition is negligible and cycloaddition proceeds smoothly, while in the aliphatic examples studied here, this competition supersedes carbonyl ylide formation. The exact mechanistic details of this reactivity crossover are still uncertain at this point. We are continuing to explore the scope, generality, and synthetic applications of the rhodium(II) acetate induced cyclization–cycloaddition methodology and will report additional findings at a later date.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were run on a Perkin-Elmer Model 283 infrared spectrometer. Proton NMR spectra were obtained on a Varian EM-390 and a General Electric QE 300 spectrometer. ^{13}C NMR spectra were recorded on a GE QE 300 spectrometer. Microanalyses were performed at Atlantic Microlabs, Atlanta, GA. Mass spectra were determined with a VG MM-7070S mass spectrometer at an ionizing voltage of 70 eV.

Preparation of 3-Butenyl *cis*-2-(Diazoacetyl)cyclopentanecarboxylate (4). To a solution containing 25 g of ethyl 2-oxocyclohexanecarboxylate in 75 mL of chloroform at 0 °C was added 23.5 g of bromine. After being stirred overnight, the solution was washed with a saturated sodium bicarbonate solution and brine and then dried over anhydrous magnesium sulfate. Evaporation of the solvent under reduced pressure afforded ethyl 5-bromo-2-oxocyclohexanecarboxylate. This material was added dropwise to an ice-cold solution containing 35 g of potassium hydroxide in 200 mL of water. After the addition was complete, the solution was stirred for 2 h and was extracted with ether. The aqueous phase was acidified with a 4.0 M hydrochloric acid solution and extracted with ether. The ethereal solution was dried over anhydrous magnesium sulfate and evaporated under reduced pressure to give a yellow oil, which crystallized on standing to give *cis*-cyclopentane-1,2-dicarboxylic acid as colorless crystals in 65% yield: mp 139–140 °C; IR (KBr) 2990, 2890, 1740, 1660, 1455, 1380, 1305, 1190, 1105, and 1030 cm^{-1}; ^1H NMR (acetone-d_6, 90 MHz) δ 1.32–2.12 (m, 6 H), 2.70–3.14 (m, 2 H), and 6.95 (br s, 2 H).

A solution containing 1.58 g of the diacid in 100 mL of acetic anhydride was heated at reflux for 10 h. The excess acetic anhydride was removed by distillation under reduced pressure. The oily residue was distilled to give *cis*-cyclopentane-1,2-dicarboxylic anhydride[52] in 85% yield as a colorless oil; bp 85–90 °C (0.5 mm); ^1H NMR (CCl_4, 90 MHz) δ 1.20–2.65 (m, 6 H) and 3.25–3.48 (m, 2 H).

A solution containing 1.4 g of the above anhydride and 3-buten-1-ol in 10 mL of pyridine and 30 mL of benzene was heated at 100 °C for 2 h. Upon cooling, the solution was poured into

(50) The possibility also exists that epimerization about the benzoyl group occurs first and this is followed by a subsequent internal addition to the π-bond.

(51) For related intramolecular cyclopropanations, see: Hirao, K.; Miura, H.; Hoshino, H.; Yonemitsu, O. *Tetrahedron Lett.* **1976**, 3895. Freeman, P. K.; Stevenson, B. K.; Balls, D. M.; Jones, D. H. *J. Org. Chem.* **1974**, *39*, 546. Nickon, A.; Kwasnick, H.; Schwartz, T.; Williams, R. O.; DiGiorgio, J. B. *J. Am. Chem. Soc.* **1965**, *87*, 1616.

(52) Birch, S. F.; Dean, R. A.; Hunter, N. J.; Whitehead, E. V. *J. Org. Chem.* **1955**, *20*, 1178.

an ice–water mixture, acidified with concentrated hydrochloric acid, and extracted with chloroform. The combined chloroform extracts were washed with a 5% aqueous sodium carbonate solution. Acidification of the aqueous solution with hydrochloric acid followed by extraction with chloroform gave 3-butenyl *cis*-2-carboxycyclopentanecarboxylate in 85% yield as a crystalline solid: mp 76–77 °C; IR (KBr) 2960, 1740, 1710, 1645, 1190, 1020, and 920 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 1.30–2.15 (m, 6 H), 2.30 (q, 2 H, 7.5 Hz), 2.88–3.14 (m, 2 H), 4.21 (t, 2 H, 7.5 Hz), 4.92–5.21 (m, 2 H), 5.48–6.00 (m, 1 H), and 9.88 (br s, 1 H). Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.17; H, 7.43.

A solution containing 212 mg of the above ester and 1.5 mmol of thionyl chloride was heated at reflux for 1 h with the exclusion of moisture until the evolution of gas had ceased. The excess thionyl chloride was removed by distillation under reduced pressure to give 3-butenyl *cis*-2-(chlorocarbonyl)cyclopentanecarboxylate in 98% yield as a colorless oil: ^1H NMR (CCl_4, 60 MHz) δ 1.52–2.10 (m, 6 H), 2.28 (q, 2 H, J = 6.0 Hz), 2.79–3.42 (m, 2 H), 4.01 (t, 2 H, J = 6.0 Hz), 4.72–5.04 (m, 2 H), and 5.28–5.98 (m, 1 H).

A solution containing 143 mg of the above chloride in 40 mL of ether was added dropwise to a solution containing 75 mmol of diazomethane in 250 mL of ether at 0 °C. The solution was allowed to warm to room temperature overnight. The solvent was removed by evaporation under reduced pressure, and the residue was subjected to silica gel chromatography using an ethyl acetate–hexane mixture as the eluent to give 3-butenyl *cis*-2-(diazoacetyl)cyclopentanecarboxylate (**4**) in 85% yield as a yellow oil: IR (neat) 2950, 2870, 2130, 1745, 1650, 1460, 1365, 1355, 1200, and 1050 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 1.68–2.08 (m, 6 H), 2.30 (q, 2 H, J = 6.0 Hz), 2.68–3.18 (m, 2 H), 4.06 (t, 2 H), 4.91–5.20 (m, 2 H), 5.26 (s, 1 H), and 5.50–5.96 (m, 1 H).

Treatment of this material with rhodium(II) acetate gave rise to a complex mixture of products, which resisted all attempts at separation and characterization. Examination of the crude NMR spectrum indicated that the olefinic hydrogens were still present.

Preparation of 3-Butenyl *endo,endo*-3-(Diazoacetyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (5). A sample of 3-butenyl *endo,endo*-3-carboxybicyclo[2.2.1]hept-5-ene-2-carboxylate was obtained in 90% yield from the known anhydride:[53] IR (neat) 3100, 2970, 1750, 1720, 1640, 1430, 1355, 1255, 1225, 1180, 1150, 1075, 930, 870, and 705 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 1.45 (q, 2 H, J = 6.0 Hz), 2.35 (q, 2 H, J = 6.0 Hz), 3.08–3.38 (m, 4 H), 4.05 (t, 2 H, J = 6.0 Hz), 5.00–5.31 (m, 2 H), 5.55–6.08 (m, 1 H), 6.22 (s, 2 H), and 10.98 (s, 1 H). Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.08, H, 6.83. Found: C, 65.94; H, 6.71.

This material was converted with thionyl chloride to 3-butenyl *endo,endo*-3-(chlorocarbonyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate in 98% yield in a manner analogous to that described above: IR (neat) 3090, 2990, 1745, 1715, 1650, 1430, 1345, 1260, 1180, 1080, 925, 795, and 770 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 1.40 (q, 2 H, J = 6.0 Hz), 2.30 (q, 2 H, J = 6.0 Hz), 3.05–3.42 (m, 3 H), 3.58–3.82 (m, 1 H), 4.02 (t, 2 H, J = 6.0 Hz), 4.93–5.22 (m, 2 H), 5.49–5.96 (m, 1 H), and 6.04–6.38 (m, 2 H).

The acid chloride was converted to 3-butenyl *endo,endo*-3-(diazoacetyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (**5**) (65% yield) as a yellow solid: mp 49–50 °C; IR (KBr) 3070, 2960, 2090, 1730, 1640, 1370, 1345, 1180, 1140, 1035, and 910 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 0.98–1.41 (m, 2 H), 2.15 (q, 2 H, J = 7.0 Hz), 2.71–3.40 (m, 4 H), 3.76 (t, 2 H, J = 7.0 Hz), 4.62–5.00 (m, 2 H), 5.08 (s, 1 H), and 5.20–6.18 (m, 3 H).

Treatment of this material with rhodium(II) acetate gave rise to a complex mixture of compounds, which could not be separated after extensive silica gel chromatography. Examination of the crude NMR spectrum indicated that the olefinic hydrogens were still present.

Preparation and Rhodium(II) Acetate Catalyzed Reaction of 2-Diazo-1-[2-[(2-propenyloxy)methyl]phenyl]ethanone (7). A solution containing 1.5 g of allyl alcohol in 25 mL of tetrahydrofuran was treated with 0.74 g of sodium hydride over 10 min at room temperature. The mixture was stirred for an additional 30 min, treated with 5.0 g of *o*-bromobenzyl bromide, and stirred for another 3 h. The solution was quenched with water, and the organic layer was washed with a saturated brine solution and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, leaving behind a residue, which was distilled at 82 °C (0.1 mm) to give 4.2 g (92%) of 1-bromo-2-[(2-propenyloxy)methyl]benzene as a clear liquid: IR (neat) 3080, 2860, 1660, 1610, 1585, 1450, 1100, 1025, 940, and 760 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 4.14 (d, 2 H, J = 5.5 Hz), 4.62 (s, 2 H), 5.21 (dd, 1 H, J = 10.3 and 0.9 Hz), 5.40 (dd, 1 H, J = 17.5 and 1.2 Hz), 6.02 (m, 1 H), 7.13–7.57 (m, 4 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 71.4, 71.7, 117.2, 122.6, 127.4, 128.8, 129.0, 132.5, 134.6, and 137.8.

A sample of 2-[(2-propenyloxy)methyl]benzoic acid (84%) was obtained in a manner analogous to that described for the methoxy derivative **15** (vide infra): mp 49–50 °C; IR (KBr) 2850–3100, 1695, 1585, 1410, 1270, 1080, and 780 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 4.17 (d, 2 H, J = 10.4 Hz), 5.01 (s, 2 H), 5.25 (d, 1 H, J = 10.3 Hz), 5.39 (d, 1 H, J = 17.9 Hz), 6.03 (m, 1 H), 7.35–8.12 (m, 4 H), 11.99 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 70.2, 71.9, 117.1, 127.1, 127.7, 131.5, 133.3, 134.6, 141.7, and 172.6; UV (95% ethanol) 278 (ϵ 830) and 232 nm (6400).

This material was converted to 2-diazo-1-[2-[(2-propenyloxy)methyl]phenyl]ethanone (**7**) in 84% yield: IR (neat) 3080, 2850, 2100, 1720, 1620, 1355, 1220, 1140, 1080, 1010, and 735 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 4.07 (d, 2 H, J = 5.7 Hz), 4.76 (s, 2 H), 5.19 (dd, 1 H, J = 10.3 and 1.0 Hz), 5.31 (dd, 1 H, J = 17.0 and 1.4 Hz), 5.75 (s, 1 H), 5.95 (m, 1 H), 7.28–7.61 (m, 4 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 56.2, 69.6, 71.7, 117.0, 127.2, 127.3, 128.8, 131.2, 134.6, 136.5, and 137.6; UV (95% ethanol) 290 (ϵ 10 000) and 254 nm (9000).

Treatment of **7** with rhodium(II) acetate gave two products, which could be separated by silica gel chromatography. The major component (43%) was assigned as 3-allyl-2-isochroman-4-one (**9**) on the basis of its spectral properties: IR (neat) 3075, 2955, 2810, 1700, 1635, 1605, 1290, 1110, 925, and 760 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 2.60 (m, 1 H), 2.83 (m, 1 H), 4.20 (dd, 1 H, J = 8.0 and 3.8 Hz), 4.88 (d, 1 H, 15.5 Hz), 4.92 (d, 1 H, J = 15.5 Hz), 5.11 (d, 1 H, J = 10.3 Hz), 5.19 (d, 1 H, J = 17.3 Hz), 5.91 (m, 1 H), 7.17–7.55 (m, 3 H) and 8.01 (m, 1 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 34.4, 66.9, 81.7, 117.6, 124.3, 126.7, 127.7, 129.5, 133.9, 134.0, 141.9, and 194.8; UV (95% ethanol) 292 (ϵ 1500) and 250 nm (11 000); *m/e* 188, 147, 131, 119, 103, 91, and 77; HRMS calcd for $C_{12}H_{12}O_2$ 188.0837, found 188.0838.

The minor product obtained (35%) was assigned as 2,3-dihydro-3-(2-propenyloxy)-1*H*-inden-1-one (**10**): IR (neat) 3085, 2930, 2865, 1725, 1655, 1615, 1470, 1340, 1290, 985, and 775 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 2.66 (dd, 1 H, J = 18.6 and 2.9 Hz), 2.99 (dd, 1 H, J = 18.6 and 6.4 Hz), 4.17 (br s, 2 H), 5.07 (dd, 1 H, J = 6.4 and 2.7 Hz), 5.16 (dd, 1 H, J = 10.3 and 1.1), 5.27 (dd, 1 H, J = 17.5 and 1.4 Hz), 5.98 (m, 1 H), 7.34–7.75 (m, 4 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 44.1, 70.7, 74.7, 117.6, 123.2, 126.5, 129.5, 134.4, 134.9, 136.8, 153.4, and 202.8; UV (95% ethanol) 286 (ϵ 1400) and 246 nm (10 000); *m/e* 188, 146, 131, 119, 103, 91, and 77; HRMS calcd for $C_{12}H_{12}O_2$ 188.0837, found 188.0836.

Preparation and Rhodium(II) Acetate Catalyzed Reaction of 2-Diazo-1-[2-[(2-propenylthio)methyl]phenyl]ethanone (11). A solution containing 1 mL of allyl mercaptan in 20 mL of tetrahydrofuran was treated with 0.36 of sodium hydride over 10 min at room temperature. The mixture was stirred for an additional 1 h and was then treated with 2.2 g of *o*-bromobenzyl bromide. The mixture was stirred for 6 h and quenched with water, and the organic layer was washed with a saturated brine solution and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, leaving behind a residue, which was distilled at 98 °C (0.1 mm) to give 1.9 g (88%) of 1-bromo-2-[(2-propenylthio)methyl]benzene as a clear liquid: IR (neat) 3080, 3065, 3010, 2990, 2910, 1640, 1575, 1470, 1440, 1230, 1025, 925, 750, and 665 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 3.10 (d, 2 H, J = 6.8 Hz), 3.77 (s, 2 H), 5.16 (d, 1 H, J = 10.4 Hz), 5.19 (d, 1 H, J = 1.2 Hz), 5.82 (m, 1 H), 7.05–7.56 (m, 4 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 34.7, 35.5, 117.5, 124.7, 128.6, 130.8, 133.2, 134.3, and 137.8.

A sample of 2-[(2-propenylthio)methyl]benzoic acid (78%) was obtained in a manner analogous to that described for carboxylic acid **15** (vide infra): mp 69–70 °C; IR (KBr) 2800–3080, 2650, 1690, 1575, 1410, 1300, 1270, 915, 780, 715, and 665 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 3.07 (d, 2 H, J = 7.1 Hz), 4.12 (s, 2 H), 5.12

(53) Diels, O.; Alder, K. *Justus Liebigs Ann. Chem.* **1928**, *460*, 98.

(d, 1 H, J = 10.9 Hz), 5.15 (d, 1 H, J = 1.0 Hz), 5.81 (m, 1 H), 7.31–7.51 (m, 3 H), 8.06 (d, 1 H, J = 9.1 Hz); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 33.4, 35.4, 117.2, 127.1, 128.3, 131.2, 132.1, 132.7, 134.5, 141.5, and 172.9; UV (95% ethanol) 280 (ϵ 1600) and 226 nm (13 000).

This material was converted to 2-diazo-1-[2-[(2-propenylthio)methyl]phenyl]ethanone (**11**) in 86% yield: IR (neat) 3075, 2920, 2100, 1725, 1620, 1350, 1220, 1015, 775, and 665 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 3.03 (d, 2 H, J = 6.9 Hz), 3.91 (s, 2 H), 5.03 (d, 1 H, J = 10.6 Hz), 5.09 (d, 1 H, J = 4.2 Hz), 5.75 (m, 2 H), 7.20–7.36 (m, 4 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 32.5, 35.0, 56.6, 117.2, 127.0, 127.7, 130.7, 130.8, 131.1, 134.3, 137.5, and 189.6; UV (95% ethanol) 292 (ϵ 11 000) and 252 nm (9000).

Treatment of **11** with rhodium(II) acetate gave two products, which were isolated by silica gel chromatography. The major component (89%) was assigned as 3-allyl-2-isothiochroman-4-one (**13**) on the basis of its spectral properties: IR (neat) 3080, 2990, 2920, 1690, 1645, 1605, 1490, 1455, 1415, 1305, 1275, 1255, 1000, 925, 780, and 745 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 2.43 (m, 1 H), 2.76 (m, 1 H), 3.58 (t, 1 H, J = 6.9 Hz), 3.72 (d, 1 H, J = 16.8 Hz), 4.00 (d, 1 H, J = 16.8 Hz), 5.03 (d, 1 H, J = 9.1 Hz), 5.09 (s, 1 H), 5.83 (m, 1 H), 7.13–7.26 (m, 3 H), 8.01 (d, 1 H, 9.0 Hz); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 29.3, 33.1, 47.5, 117.7, 127.4, 127.8, 129.1, 132.4, 132.6, 134.4, 141.0, and 192.5; UV (95% ethanol) 292 (ϵ 1700) and 244 nm (10 000); m/e 204, 163, 135, 118, 90, and 77; HRMS calcd for $C_{12}H_{12}OS$ 204.0611, found 204.0608.

The minor product (10%) obtained was a yellow oil and was assigned as 2,3-dihydro-3-(2-propenylthio)-1*H*-inden-1-one (**14**): IR (neat) 3090, 2915, 1725, 1645, 1610, 1470, 1295, 1280, 1230, 930, and 780 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 2.73 (dd, 1 H, J = 19.3 and 2.9 Hz), 3.12 (m, 3 H), 4.43 (dd, 1 H, J = 7.3 and 2.6 Hz), 5.06 (d, 1 H, J = 10.7 Hz), 5.10 (s, 1 H), 5.81 (m, 1 H), 7.32–7.72 (m, 4 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 34.6, 40.3, 46.2, 117.7, 123.4, 126.7, 128.5, 134.1, 135.1, 137.0, 154.5, and 203.9; UV (95% ethanol) 250 nm (ϵ 8000); m/e 204, 162, 131, 103, and 77; HRMS calcd for $C_{12}H_{12}OS$ 204.0609, found 204.0608.

Preparation and Rhodium(II) Acetate Catalyzed Reaction of 3-Butenyl 5-Diazo-4-oxopentanoate (15). A solution containing 0.86 mL of 1-buten-4-ol and 1.0 g of succinic anhydride in 3 mL of benzene and 1 mL of pyridine was heated at reflux for 2 h. The reaction mixture was taken up in 50 mL of ether, washed with 25 mL of a 10% hydrochloric acid solution and once with a saturated brine solution, and then dried over sodium sulfate. The solvent was removed under reduced pressure, and the resulting residue contained 1.36 g (79%) of butanedioic acid mono-3-butenyl ester as a clear oil: IR (neat) 3085, 2980, 1740, 1720, 1425, 1180, and 930 cm^{-1}; ^{1}H NMR (90 MHz, CCl_4) δ 2.15–2.50 (m, 2 H), 2.54 (br s, 4 H), 4.08 (t, 2 H, J = 7.0 Hz), 4.90–5.23 (m, 2 H), 5.5–6.0 (m, 1 H), and 11.40 (s, 1 H). This material was treated with 0.61 mL of methyl chloroformate and 1.1 mL of triethylamine. The resulting white suspension was stirred at 25 °C for 5 h and was then filtered. The crude anhydride was treated with an excess of freshly prepared diazomethane at 0 °C, and the solution was then allowed to warm to 25 °C over a 12-h interval. The solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography using a 3:1 hexane–ethyl acetate mixture as the eluent to give 0.98 g (63%) of 3-butenyl 5-diazo-4-oxopentanoate (**15**) as a clear oil: IR (neat) 3095, 2970, 2930, 2120, 1740, 1650, 1390, 1360, 1180, and 800 cm^{-1}; ^{1}H NMR (90 MHz, CCl_4) δ 2.35 (q, 2 H, J = 6.8 Hz), 2.55 (s, 4 H), 4.10 (t, 2 H, J = 6.8 Hz), 4.95–5.25 (m, 2 H), 5.32 (s, 1 H), and 5.55–6.03 (m, 1 H).

A solution containing 344 mg of **15** in 50 mL of dry benzene was treated with 5 mg of rhodium(II) acetate. Vigorous nitrogen evolution was observed, and the yellow solution was then stirred for 1 h at room temperature, during which time it slowly turned green. The reaction mixture was filtered, and the solvent was removed under reduced pressure. The crude yellow oil was subjected to silica gel chromatography using a 3:1 hexane–ethyl acetate mixture as the eluent. The major material isolated from the column contained 152 mg (53% yield) of a clear oil, whose structure was assigned as 3-butenyl 5-hydroxy-4-oxopentanoate (**19**) on the basis of its spectral properties: IR (neat) 3500, 3100, 2980, 2940, 1730, 1645, 1415, 1360, 1205, 1105, 1080, 995, and 925 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.36 (q, 2 H, J = 7.0 Hz), 2.68 (s, 4 H), 2.99 (t, 1 H, J = 4.9 Hz), 4.12 (t, 2 H, J = 6.7 Hz), 4.30 (d, 2 H, J = 4.9 Hz), 5.01–5.17 (m, 2 H), and 5.66–5.84 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.6, 32.7, 32.8, 63.8, 68.1, 117.2, 133.7, 172.0, and 207.9; HRMS calcd for $C_9H_{14}O_4$ 186.0892, found 186.0889.

Preparation and Rhodium(II) Acetate Catalyzed Reaction of 1-Diazo-9-decene-2,5-dione (20). A sample of 4-oxo-8-nonenoic acid was prepared in 68% yield from the reaction of succinic anhydride and the Grignard reagent derived from 5-bromo-1-pentene: IR (neat) 3090, 2950, 2680, 1720, 1650, 1420, 1380, 1225, 1180, 1005, 925, and 850 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.15–2.30 (m, 6 H), 2.35–3.00 (m, 4 H), 4.93 (br s, 1 H), 5.10 (br s, 1 H, J = 6.0 Hz), 5.50–6.05 (m, 1 H), and 9.50 (br s, 1 H). This material was converted to diazo dione **20** in 41% yield: IR (neat) 3100, 2950, 2115, 1785, 1715, 1640, 1440, 1380, 1325, 1215, 1155, 1000, and 920 cm^{-1}; ^{1}H NMR (90 MHz, CCl_4) δ 1.67 (q, 2 H, J = 6.0 Hz), 2.02 (q, 2 H, J = 6.0 Hz), 2.40 (t, 2 H, J = 6.0 Hz), 2.54 (t, 2 H, J = 8.6 Hz), 2.58 (t, 2 H, J = 9.0 Hz), 4.90 (s, 1 H), 5.05 (br d, 1 H, J = 6.0 Hz), 5.40 (s, 1 H), and 5.50–6.05 (m, 1 H).

A solution containing 394 mg of **20** in 25 mL of benzene was treated with 5 mg of rhodium(II) acetate for 6 h at 25 °C. The solution was filtered and concentrated under reduced pressure. The crude oil was subjected to silica gel chromatography using a 3:1 hexane–ethyl acetate mixture to give 253 mg (75%) of a clear oil, whose structure was assigned as hexahydro-1*H*-3a,7-epoxyazulen-6(7*H*)-one (**22**) on the basis of its spectral data: IR (neat) 2960, 2880, 1725, 1455, 1420, 1235, 1085, 1040, 935, 900, and 815 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.35–2.04 (m, 8 H), 2.09–2.52 (m, 5 H), and 4.24 (d, 1 H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.9, 32.7, 33.8, 34.0, 36.8, 39.0, 44.8, 84.0, 92.5, and 209.4; HRMS calcd for $C_{10}H_{14}O_2$ 166.0988, found 166.0994.

Preparation and Rhodium(II) Acetate Catalyzed Reaction of *endo,endo*-3-Benzoyl-2-(diazoacetyl)bicyclo[2.2.1]hept-5-ene (23). To a solution containing 1.67 g of *endo*-2,3-norbornene dicarboxylic anhydride in 100 mL of tetrahydrofuran at −78 °C was added 10 mmol of the Grignard reagent prepared from bromobenzene. The mixture was allowed to warm to 25 °C over 3 h and was then poured onto 150 mL of a 10% hydrochloric acid solution. The aqueous mixture was extracted with ether. The ether extracts were washed with 50 mL of a 1.0 M sodium hydroxide solution, and the basic layer was acidified with 100 mL of a 1.0 M hydrochloric acid solution and extracted with ether. The ether extracts were dried over sodium sulfate, and the solution was concentrated under reduced pressure to give *endo,endo*-3-benzoylbicyclo[2.2.1]hept-5-ene-2-carboxylic acid as a white solid in 36% yield: mp 139–140 °C; IR (KBr) 3100, 3000, 2960, 2900, 2740, 2680, 1750, 1690, 1600, 1580, 1495, 1450, 1410, 1340, 1330, 1260, 1230, 1175, 970, 940, 920, 885, 845, 815, 755, 725, 700, and 645 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.43 (br s, 2 H), 3.03–3.23 (m, 1 H), 3.23–3.40 (m, 1 H), 3.45 (dd, 1 H, J = 9.9 and 4.2 Hz), 3.87 (dd, 1 H, J = 9.9 and 4.2 Hz), 5.15 (dd, 1 H, J = 6.0 and 3.0 Hz), 6.10 (dd, 1 H, J = 6.0 and 3.0 Hz), and 7.20–7.58 (m, 5 H).

A solution containing 1.0 g of the above keto acid in 50 mL of anhydrous ether was treated with 0.8 mL of methyl chloroformate and 1.0 mL of triethylamine. The precipitated triethylamine hydrochloride was filtered, and the crude anhydride was treated with freshly prepared diazomethane at 0 °C. The solution was allowed to warm to 25 °C over a 12-h period. The solvent was removed under reduced pressure, and the crude residue was subjected to silica gel chromatography using a 3:1 hexane–ethyl acetate mixture to give *endo,endo*-3-benzoyl-2-(diazoacetyl)bicyclo[2.2.1]hept-5-ene (**23**) in 36% yield as a clear oil: IR (neat) 3090, 3000, 2970, 2140, 1750, 1680, 1640, 1600, 1580, 1450, 1350, 1260, 1210, 1100, 1055, 1020, 985, 920, 790, 760, 695, and 660 cm^{-1}; ^{1}H NMR (90 MHz, CCl_4) δ 1.38 (d, 1 H, J = 9.0 Hz), 1.68 (d, 1 H, J = 9.0 Hz), 2.93–3.32 (m, 2 H), 3.50–4.10 (m, 2 H), 5.35 (s, 1 H), 6.03–6.28 (m, 1 H), 6.28–6.52 (m, 1 H), 7.25–7.70 (m, 3 H), and 7.90–8.23 (m, 2 H).

A solution containing 103 mg of **23** in 5 mL of benzene was stirred at 25 °C for 4 h in the presence of 2 mg of rhodium(II) acetate and 1.2 equiv of DMAD. The solution was filtered, and the solvent was removed under reduced pressure to give a crude oil, which was subjected to silica gel chromatography using a 3:1 hexane–ethyl acetate mixture. The major fraction contained 68 mg (74%) of a clear oil, whose structure was assigned as 5-benzoylhexahydro-1,3-methanocyclopropa[*c,d*]pentalen-2(1*H*)-one

(26) on the basis of its spectral properties: IR (neat) 3080, 3010, 2920, 1730, 1680, 1600, 1585, 1450, 1315, 1295, 1265, 1235, 1200, 1010, 890, 770, and 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.68 (d, 1 H, J = 9.9 Hz), 1.77 (d, 1 H, J = 9.9 Hz), 2.06-2.18 (m, 1 H), 2.23-2.37 (m, 1 H), 2.60-2.70 (m, 1 H), 2.84 (br s, 1 H), 2.91 (br d, 2 H, J = 4.5 Hz), 3.45 (s, 1 H), 7.47 (t, 2 H, J = 8.0 Hz), 7.56 (t, 1 H, J = 7.0 Hz), and 7.94 (d, 2 H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 34.2, 35.6, 38.6, 39.0, 39.9, 46.1, 47.0, 128.5, 128.7, 133.3, 135.2, 196.8, and 213; HRMS calcd for $C_{16}H_{14}O_2$ 238.0994, found 238.1001.

Preparation and Rhodium(II) Acetate Catalyzed Reaction of *cis*-2-Benzoyl-1-(diazoacetyl)cyclopentane (28). A solution containing 1.03 g of *cis*-2-benzoylcyclopentanecarboxylic acid[56] and 0.51 mL of methyl chloroformate in 30 mL of ether and 15 mL of tetrahydrofuran was treated with 0.92 mL of triethylamine. After being stirred for 2 h under a nitrogen atmosphere, the solution was filtered and was then treated with an excess of diazomethane in ether. The reaction mixture was slowly allowed to warm from 0 °C to room temperature over a 12-h interval. The solvent was removed under reduced pressure, and the resulting oil was purified via silica gel flash chromatography using a 3:1 hexane-ethyl acetate mixture as the eluent. The first component eluted from the column contained 0.8 g of hexahydro-2-oxa-3-methoxy-3-phenylpentalen-1-one: IR (neat) 2960, 2890, 1800, 1775, 1455, 1265, 1175, 960, 770, and 710 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.1-1.4 (m, 3 H), 1.8-2.0 (m, 3 H), 3.13 (dt, 1 H, J = 7.4 Hz and 7.2 Hz), 3.32 (dt, 1 H, J = 8.4 and 3.3 Hz), 3.50 (s, 3 H), and 7.2-7.4 (m, 5 H).

The second material eluted from the column contained 0.17 g (15%) of *cis*-2-benzoyl-1-(diazoacetyl)cyclopentane (**28**): IR (neat) 2980, 2130, 1680, 1635, 1450, 1375, and 1225 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.60-2.10 (m, 6 H), 3.01 (q, 1 H, J = 8.0 Hz), 4.01 (dt, 1 H, J = 7.7 and 7.0 Hz), 5.20 (s, 1 H), 7.33-7.48 (m, 3 H), and 7.82-7.85 (m, 2 H).

To a solution containing 90 mg of *cis*-2-benzoyl-1-(diazoacetyl)cyclopentane (**28**), 0.05 mL of dimethyl acetylenedicarboxylate, and 5 mL of benzene was added 3 mg of rhodium(II) acetate. The solution was stirred at room temperature under a nitrogen atmosphere for 4.5 h. After filtration, the solvent was removed under reduced pressure and the resulting residue was purified via silica gel flash chromatography using a 10:1 hexane-ethyl acetate mixture as the eluent. The major fraction contained a yellow oil (75%), whose structure was assigned as dimethyl 1,2,3,3a,4,7,8,8a-octahydro-4-phenyl-8-oxo-4,7-epoxyazulene-5,6-dicarboxylate (**30**): IR (neat) 2980, 1730, 1660, 1450, 1435, 1330, 1255, 1145, 1020, and 755 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.80-1.70 (m, 4 H), 1.9-2.1 (m, 2 H), 3.14 (ddd, 1 H, J = 8.7, 8.6, and 5.5 Hz), 3.2-3.4 (m, 1 H), 3.65 (s, 3 H), 3.74 (s, 3 H), 5.10 (s, 1 H), and 7.2-7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.4, 28.7, 28.9, 46.1, 46.8, 52.6, 86.0, 92.9, 125.4, 128.1, 128.3, 131.7, 137.5, 151.2, 160.8, 164.4, and 202.2; UV (95% ethanol) 240 (ϵ 7100) and 322 nm (560); HRMS calcd for $C_{20}H_{20}O_6$ 356.1259, found 356.1246.

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Synthesis of Indolo[2,3-*a*]pyrrolo[3,4-*c*]carbazoles by Double Fischer Indolizations

Jan Bergman* and Benjamin Pelcman

Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

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A synthesis of indolo[2,3-*a*]pyrrolo[3,4-*c*]carbazoles (**16**) based on a double Fischer indolization of the bis(phenylhydrazones) (**10**), employing polyphosphoric acid trimethylsilyl ester (PPSE) as the cyclization agent, is described. The bis(phenylhydrazones) (**10**) were prepared by a Diels-Alder reaction of 2,3-bis[(trimethylsilyl)oxy]butadiene (**6**) with the dienophiles **7** followed by reaction with the appropriate substituted phenylhydrazines (**9**). By use of this methodology arcyriaflavin A (**4a**) and the aglycon (**16d**) of the antitumor alkaloid rebeccamycin as well as a number of analogues of this class of alkaloids have been prepared.

The classical Fischer indole synthesis has been and still is the most frequently used method for the preparation of indoles.[1] Its versatility has continuously been expanded by the introduction of a wide range of new catalysts, which has allowed construction of more sensitive substances and improved yields and selectivity.

In our efforts[2] to explore new routes[3] to indolocarbazole alkaloids,[4-9] such as the protein kinase inhibitors staurosporine (**1**)[10] and K-254a (**2**),[11] the antitumoral rebeccamycin (**3**),[12] and the arcyriaflavins (**4**),[4,13] it was desirable

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