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Rhodium Carbenoid Mediated Cyclizations of *o*-Alkynyl-Substituted α-Diazoacetophenones

Albert Padwa,* Keith E. Krumpe, and Jamal M. Kassir

Department of Chemistry, Emory University, Atlanta, Georgia 30322

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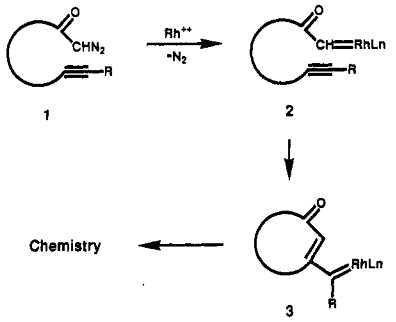
o-Alkynyl-substituted α-diazoacetophenones undergo facile cyclization to indenone derivatives upon treatment with catalytic quantities of Rh(II) carboxylates. A variety of structural influences were encountered by varying the nature of the substituent group attached to the alkyne carbon atom. The cyclization reaction involves addition of a rhodium stabilized carbenoid onto the acetylenic π-bond to generate a vinyl carbenoid. The vinyl carbenoid was found to undergo both CH and CC migration as well as δ-CH insertion into the alkyl backbone. Different catalysts were shown to result in significant variation in the product ratios for these reactions. Treatment of *o*-(5-(allyloxy)-1-pentynyl)-α-diazoacetophenone with rhodium(II) mandelate afforded 2-(2-propen-1-yl)-2-(1-oxo-1*H*-indenyl)-2,3,4,5-tetrahydrofuran in high yield. The formation of this compound involves initial formation of a vinyl carbenoid which reacts with the neighboring oxygen atom to give an oxonium ylide which subsequently undergoes a 2,3-sigmatropic rearrangement. When 2-ethynyl-α-diazoacetophenone is used, only products derived from 6-*endo* closure are observed. Substituted o-alkynyl α-diazoacetophenones give products derived from 5-*exo* cyclization. The mode of ring closure is controlled by both steric and electronic factors.

In recent years catalytic transition-metal-mediated reactions have provided organic chemists with exceptionally fertile ground for designing and developing new stereoselective bond constructions for application in organic synthesis.[1–25] In developing the chemistry of organic molecules coordinated onto transition-metal centers, the reactions of α-diazo ketones have played an important role.[26–28]

Scheme I



With the advent of rhodium(II) acetate as a superior catalyst to generate transient electrophilic metal carbenoids from α-diazo carbonyl compounds,[29] intramolecular carbenoid addition[30] and insertion reactions[31–34] have assumed strategic importance in C–C bond forming reactions in organic synthesis. Far less attention has been given to the catalytic internal cyclopropenation reaction of α-diazo keto alkynes.[35] Recent work by our group[36] as well as Hoye's[37] have shown that the rhodium(II)-catalyzed re-

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(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(2) Mass, G. *Top Curr. Chem.* **1987**, *137*, 77.

(3) Doyle, M. P. *Acc. Chem. Res.* **1986**, *19*, 348; *Chem. Rev.* **1986**, *86*, 919.

(4) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081.

(5) *Tetrahedron Symposia in Print*; Semmelhack, M. F., Ed.; 1985, Vol. 42, pp 5741–5887.

(6) Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461.

(7) Deem, M. L. *Synthesis* **1982**, 701; 1972, 675.

(8) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644. Dötz, K. H.; Popall, M. *Tetrahedron* **1985**, *41*, 5797. Dötz, K. H.; Dietz, R. *Chem. Ber.* **1978**, *111*, 2517.

(9) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1990; Vol. 5. Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press Inc.: Greenwich, CT, 1989; Vol. 1. McCallum, J. S.; Kunng, F.-A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346. Wulff, W. D.; Xu, Y.-C. *Tetrahedron Lett.* **1988**, *29*, 415.

(10) Boger, D. L.; Jacobson, I. C. *J. Org. Chem.* **1990**, *55*, 1919.

(11) Yamashita, A. *J. Am. Chem. Soc.* **1988**, *107*, 5823.

(12) Peterson, G. A.; Kunng, F.-A.; McCallum, J. S.; Wulff, W. D. *Tetrahedron Lett.* **1987**, *28*, 1381.

(13) Semmelhack, M. F.; Bozell, J. J.; Keller, L.; Sato, T.; Spiess, E. J.; Wu, W.; Zask, A. *Tetrahedron* **1985**, *41*, 5803.

(14) Burkhardt, E. R.; Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 2022.

(15) Alt, H. G. *J. Organomet. Chem.* **1985**, *288*, 149.

(16) Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 2055.

(17) Slough, G. A.; Deshong, P. *J. Am. Chem. Soc.* **1988**, *110*, 2575.

(18) Davidson, J. L.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2044.

(19) Heck, R. F. *J. Am. Chem. Soc.* **1964**, *86*, 1819.

(20) Bottrill, M.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 292.

(21) Corrigan, P. A.; Dickson, R. S. *Aust. J. Chem.* **1979**, *32*, 2147.

(22) Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002.

(23) Maitlis, P. M. *Acc. Chem. Res.* **1976**, *9*, 93.

(24) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 6232.

(25) Harvey, D. F.; Brown, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 7806. Harvey, D. F.; Lund, K. P. *J. Am. Chem. Soc.* **1991**, *113*, 5066.

(26) Dave, V.; Warnhoff, E. *Org. React.* (N.Y.) **1970**, *18*, 217.

(27) Wenkert, E. *Acc. Chem. Res.* **1980**, *13*, 27.

(28) Doyle, M. P. In *Catalysis of Organic Reactions*; Augustine, R. L., Ed.; Marcel Dekker: New York, 1985; Chapter 4.

(29) Hubert, A. J.; Noels, A. F.; Anciaux, A. J.; Teyssie, P. *Synthesis* **1976**, 600. Anciaux, A. J.; Hubert, A. J.; Noels, A. F.; Petinoit, N.; Teyssie, P. *J. Org. Chem.* **1980**, *45*, 695.

(30) Burke, S. D.; Grieco, P. A. *Org. React.* (N.Y.) **1979**, *26*, 361.

(31) Wenkert, E.; Davis, L. L.; Mylari, B. L.; Solomon, M. F.; daSilva, R. R.; Shulman, S.; Warnet, R. J.; Ceccherelli, P.; Curini, M.; Pellicciari, R. *J. Org. Chem.* **1982**, *47*, 3242.

(32) Taber, D. F.; Petty, E. H. *J. Org. Chem.* **1982**, *47*, 4808. Taber, D. F.; Raman, K. *J. Am. Chem. Soc.* **1983**, *105*, 5935. Taber, D. F.; Petty, E. H.; Raman, K. *J. Am. Chem. Soc.* **1985**, *107*, 196. Taber, D. F.; Ruckle, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 7686. Taber, D. F.; Hoerrner, R. S. *J. Org. Chem.* **1992**, *57*, 441.

(33) Moyer, M. P.; Feldman, P. L.; Rapoport, H. *J. Org. Chem.* **1985**, *50*, 5223.

(34) Jefford, C. W.; Zaslona, A. *Tetrahedron Lett.* **1985**, *26*, 6035.

(35) Mykytka, J. P.; Jones, W. M. *J. Am. Chem. Soc.* **1975**, *97*, 5933.

(36) (a) Padwa, A.; Austin, D. J.; Xu, S. L. *J. Org. Chem.* **1992**, *57*, 1330. (b) Padwa, A.; Krumpe, K. E.; Zhi, L. *Tetrahedron Lett.* **1989**, *30*, 2623. (c) Padwa, A.; Chiacchio, U.; Gareau, Y.; Kassir, J. M.; Krumpe, K. E.; Schoffstall, A. M. *J. Org. Chem.* **1990**, *55*, 414. (d) Padwa, A.; Krumpe, K. E.; Gareau, Y.; Chiacchio, U. *J. Org. Chem.* **1991**, *56*, 2523. (e) Padwa, A.; Austin, D. J.; Xu, S. L. *Tetrahedron Lett.* **1991**, *32*, 4103. (f) Kinder, F. R.; Padwa, A. *Tetrahedron Lett.* **1990**, *31*, 6835.

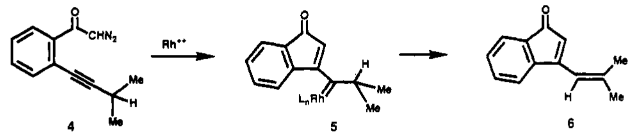
(37) (a) Hoye, T. R.; Dinsmore, C. J.; Johnson, D. S.; Korkowski, P. F. *J. Org. Chem.* **1990**, *55*, 4518. (b) Hoye, T. R.; Dinsmore, C. J. *J. Am. Chem. Soc.* **1991**, *113*, 4343. (c) Hoye, T. R.; Dinsmore, C. J. *Tetrahedron Lett.* **1991**, *32*, 3755. (d) Hoye, T. R.; Dinsmore, C. J. *Tetrahedron Lett.* **1992**, *33*, 169.

0022-3263/92/1957-4940$03.00/0

action of α-diazo ketones (1) bearing tethered alkyne units represents a powerful method for the construction of a variety of polycyclic skeletons. Exposure of 1 to a rhodium(II) catalyst results in cyclization of the α-keto carbenoid 2 to an intermediate (3) in which carbene-like reactivity has appeared on one of the original alkyne carbon atoms. A neighboring functional group present on the backbone traps the cyclized intermediate 3 via known carbene chemistry to give various products (Scheme I). The specific types of reaction that the monocyclic intermediate 3 can undergo have been of interest to us. In this paper we describe the scope of the Rh(II)-induced cyclization of a series of alkynyl substituted α-diazo ketones with emphasis on the remarkable array of chemistry that is possible from the cyclized intermediates.

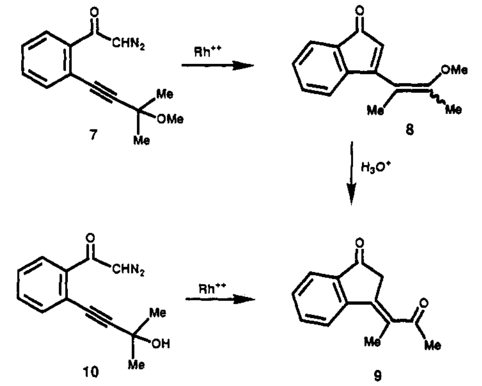
Results and Discussion

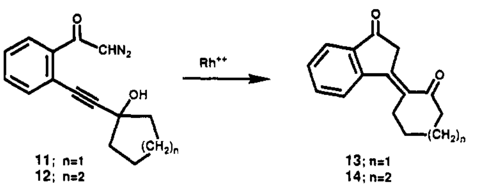
Our initial studies focused on the rhodium(II)-catalyzed reaction of *o*-alkynyl-substituted α-diazoacetophenone derivatives which contained a group capable of undergoing rearrangement. Insertions into adjacent carbon–hydrogen and carbon–carbon bonds are reactions characteristic of singlet alkyl- and dialkyl-substituted carbenes.[38] Our intention was to generate vinyl carbenoid 5 from the Rh(II)-catalyzed reaction of α-diazo ketone 4 and evaluate the facility of the 1,2-hydrogen or alkyl shift to the carbenoid center. The 1,2-shift of hydrogen in a singlet carbene to form an alkene formally involves the migration of hydrogen to a vacant π orbital.[39] It is generally assumed that the migrating group carries its electrons into the vacant orbital of the singlet carbene. The ease of migration is related to the ground-state alignment of the vacant π and σ-CH orbitals.[39,40] The ability of groups to migrate to a divalent carbon in the decomposition of diazo compounds are hydrogen > aryl > alkyl.[41] We assume that related arguments can be made for the corresponding rhodium carbenoid 5. Indeed, treatment of 4 with rhodium(II) mandelate gave indenone 6 in 97% yield.



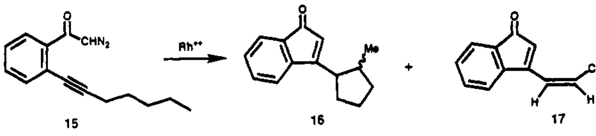
A similar reaction using α-diazo ketone 7 with the same catalyst at 25 °C afforded 82% of a 5:3 mixture of the *E*- and *Z*-enol ethers 8. No signs of the methoxy migrated product were evident in the crude reaction mixture.[42] The mixture of stereoisomers was cleanly hydrolyzed to indanone 9. This same indanone was obtained upon treatment of the related alcohol 10 with a rhodium(II) carboxylate catalyst. The preferential migration of the methyl group with both diazo ketones is undoubtedly related to the ability of the methoxy (or hydroxy) group to stabilize the developing positive charge in the transition state for the rearrangement.

The success achieved by the Rh(II)-catalyzed transformation of 10 was also extended to a series of cyclic acetylenic alcohols. Due to their convenience in preparation, the (1-hydroxycycloalkyl)ethynyl-substituted α-diazoacetophenones 11 and 12 were chosen for investigation. Treatment of these compounds with a catalytic amount of Rh(II) octanoate gave the ring-expanded indanones 13 and 14 as a 1:1 cis/trans mixture in 82 and 86% yield, respectively.





The competition between C–H insertion and the 1,2-hydrogen migration was also investigated. Treatment of α-diazoacetophenone 15 with Rh(II) mandelate in benzene at 25 °C afforded a 1:1 mixture of the δ-CH insertion product 16 (1:2 cis/trans) as well as (*Z*)-alkene 17 derived from a 1,2-hydrogen migration to the carbenoid center. The Rh(II) carboxylate mediated C–H insertion reactions of α-diazo β-keto esters into freely rotating aliphatic side chains are known to preferentially lead to five-membered-ring formation.[32] The formation of cyclopentylindenone 16 is perfectly consistent with these earlier observations. We have also discovered that these α-diazo keto alkyne insertion reactions are ligand dependent, thereby suggesting that a metalated species is involved in the product-determining step. Similar observations have been made previously.[37] By changing the catalyst from $Rh_2(man)_4$ (man = mandelate) through $Rh_2(OAc)_4$ to $Rh_2(pfb)_4$ (pfb = perfluorobutyrate), significant manipulation of the product distribution could be achieved. The data indicate that the more electron-withdrawing perfluorobutyrate ligand favors β-hydride elimination, while 1,5-insertion is favored by the more electron-donating ligands. The intermediate rhodium carbenoid is highly electron deficient at the carbon center and is further destabilized by an electron-withdrawing ligand. With this more reactive intermediate, the entropically less demanding β-hydride elimination pathway is favored. Similar findings have been reported in a very recent study.[43] Another point worth noting is the preferential formation



$Rh_2(man)_4$	50/50
$Rh_2(OAc)_4$	66/33
$Rh_2(oct)_4$	80/20
$Rh_2(pfb)_4$	10/90

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[38] Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic: New York, 1971. Jones, M., Jr., Moss, R. A., Eds. *Carbenes*; Academic: New York, 1973; Vol. 1. Moss, R. A., Jones, M., Jr., Eds. *Carbenes*; Academic: New York, 1975; Vol. 2.

[39] Jones, W. M. In *Rearrangement in Ground and Excited States*; deMayo, P., Ed.; Academic Press: New York, 1980; pp 95–160.

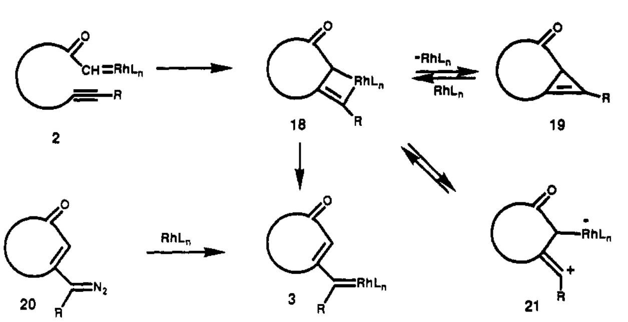
[40] Gaspar, P. P.; Hammond, G. S. In *Carbenes*; Moss, R. A., Jones, M., Jr., Eds; Academic Press: New York, 1975; Vol. 2, pp 207–362.

[41] Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1961**, *83*, 3159. Phillip, H.; Keating, J. *Tetrahedron Lett.* **1961**, 523.

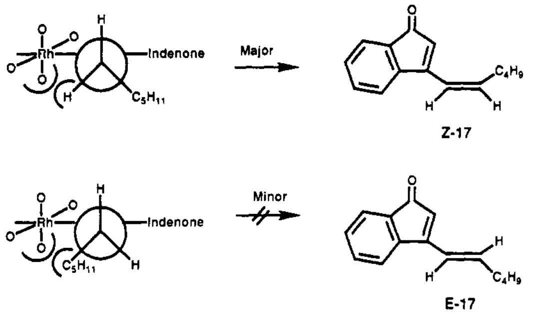
[42] Kirmse, W.; Buschoff, M. *Angew. Chem.* **1965**, *77*, 681.

[43] Taber, D. F.; Hennessy, M. J.; Louey, J. P. *J. Org. Chem.* **1992**, *57*, 436.

Scheme II

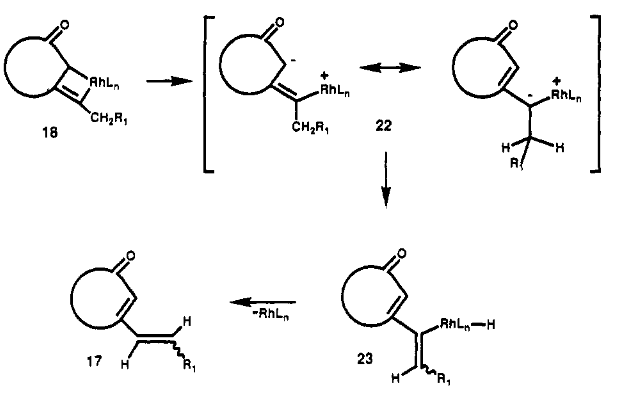


of the thermodynamically less stable *Z*-isomer **17** which is derived from the 1,2-hydrogen shift. This stereochemical result can be attributed to constraints by the face of the rhodium carboxylate on orientation of the alkyl chain for hydrogen migration in the metal carbene intermediate.[44-46]

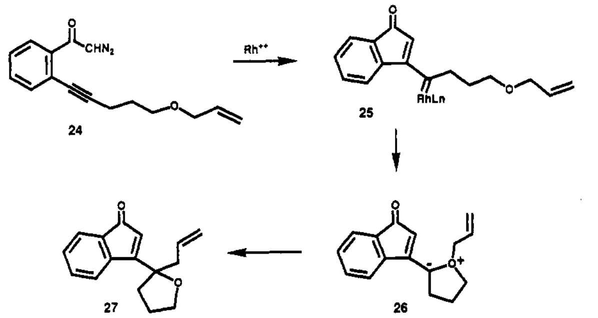


The simplest mechanism accounting for migration of the rhodium metal to the remote alkyne carbon involves a [2 + 2]-cycloaddition/cycloreversion path (i.e., **2** → **18** → **3**) (Scheme II). Other possible variations are certainly conceivable. For example, it has been reported that the distribution of products arising from the rhodium(II)-catalyzed reaction of α-diazo enones of type **20** differ from those obtained from the acetylenic ketones.[37b] This observation led to the suggestion that the results are consistent with the formation of an intermediate zwitterion of type **21**. A 1,2-hydrogen shift from **21** could easily lead to olefins related to **17**. Another conceivable path for the conversion of **15** into **17** involves formation of the rhodium-hydride species **23** (via **22**) which then undergoes reductive elimination to give **17** and regeneration of the catalyst (Scheme III). Complicating the problem is the fact that the mechanism of reaction as well as chemoselectivity is markedly influenced by the solvent used.[36a] In nonpolar solvents, rhodium migration more than likely occurs via the metallocyclobutene intermediate **18** so as to avoid charge buildup. Clearly, many intermediates may be envisioned along the pathway from **15** to **17**, and it is not an easy task to identify the mechanistic differences.

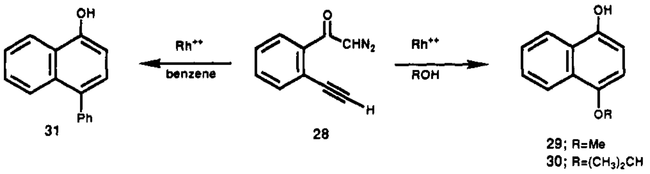
Scheme III



In earlier papers we had reported on the rhodium-induced α-diazo ketone cyclization onto a neighboring carbonyl group followed by dipolar cycloaddition of the resulting carbonyl ylide as a method for the formation of oxapolycyclic ring systems.[47] The ease with which ylide formation occurred suggested to us that a similar sequence might take place by incorporating an allyl oxy group on the tethered alkyne unit. Recent studies have shown that the metal-catalyzed reactions of α-diazo compounds with a broad selection of allylic substrates result in products derived from 2,3-sigmatropic rearrangement of intermediate allylic ylides.[48-51] Indeed, we have found that such a process occurs upon treating **24** with rhodium(II) mandelate in dichloromethane at 25 °C. The product formed in 81% yield corresponded to tetrahydrofuran **27** which can best be rationalized as proceeding via oxonium ylide **26**.



A variety of structural influences has been encountered by varying the nature of the substituent group attached to the alkyne carbon atom.[36,37] As part of our work in this area, we decided to probe the influence of the alkyne substituents on the mode of cyclization. Initial efforts focused on the rhodium(II)-catalyzed reaction of 2-ethynyl-α-diazoacetophenone (**28**). Interestingly, the reaction of **28** with Rh(II) mandelate in methanol or 2-propanol afforded naphthols **29** and **30** as the only identifiable products in good yields. When the reaction was carried out using benzene as the solvent, 4-phenyl-1-naphthol (**31**) was obtained in 70% yield.



The cyclization reaction of 3-carbomethoxy-2-ethynyl-α-diazoacetophenone (**32**) in methanol proceeded in a similar manner giving rise to a 1:1 mixture of **35** and **36**.

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(44) Shankar, B. K. R.; Shechter, H. *Tetrahedron Lett.* **1982**, *23*, 2277.

(45) Ikota, N.; Takamura, N.; Young, S. D.; Ganem, B. *Tetrahedron Lett.* **1981**, *22*, 4163.

(46) Doyle, M. P.; High, K. G.; Oon, S. M.; Osborn, A. K. *Tetrahedron Lett.* **1989**, *30*, 3049.

(47) Padwa, A.; Fryxell, G. E.; Zhi, L. *J. Am. Chem. Soc.* **1990**, *112*, 3100. Padwa, A.; Carter, S. P.; Nimmesgern, H. *J. Org. Chem.* **1986**, *51*, 1157. Padwa, A.; Carter, S. P.; Nimmesgern, H.; Stull, P. *J. Am. Chem. Soc.* **1988**, *110*, 2894. Padwa, A.; Dean, D. C.; Zhi, L. *J. Am. Chem. Soc.* **1989**, *111*, 6541. Padwa, A.; Dean, D. C. *J. Org. Chem.* **1990**, *55*, 405. Padwa, A.; Zhi, L. *J. Am. Chem. Soc.* **1990**, *112*, 2037. Padwa, A. *Acc. Chem. Res.* **1991**, *24*, 22.

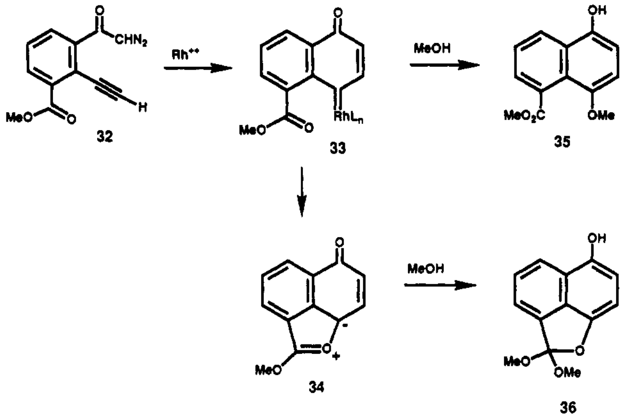
(48) Doyle, M. P.; Griffin, J. H.; Chinn, M. S.; Van Leusen, D. *J. Org. Chem.* **1984**, *49*, 1917.

(49) Pirrung, M. C.; Werner, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 6060.

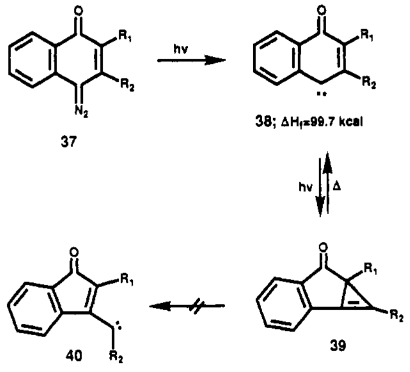
(50) Roskamp, E. J.; Johnson, C. R. *J. Am. Chem. Soc.* **1986**, *108*, 6062.

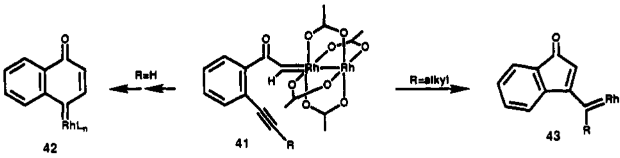
(51) Padwa, A.; Hornbuckle, S. F.; Fryxell, G. E.; Stull, P. D. *J. Org. Chem.* **1989**, *54*, 817.

The formation of **36** can be nicely accounted for in terms of the intermediacy of vinyl carbenoid **33**, which cyclizes onto the oxygen atom of the neighboring carbonyl group to give the resonance-stabilized dipole **34**. Trapping this species with methanol leads to **36**, whereas insertion of vinyl carbenoid **33** into methanol gives **35**.

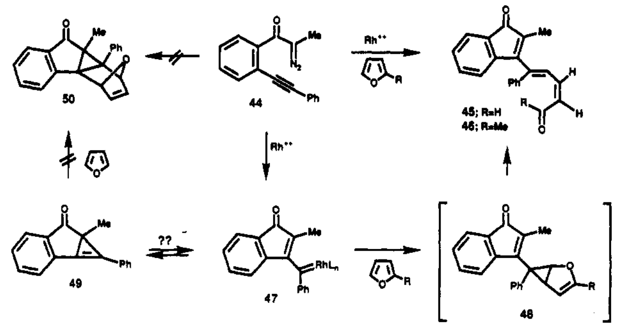


The fact that α-diazoacetophenones **28** and **32** give products derived from a six-ring vinyl carbenoid is particularly noteworthy and bears some discussion. 4-Oxocyclohexa-2,5-dienylidene **38** has recently been generated in an argon matrix at 10 K by irradiation of the corresponding diazo quinone **37**.[52] On further photolysis, carbene **38** rearranges to the highly strained bicyclo[3.1.0]hexadien-2-one (**39**). The 1,3-bridged cyclopropene **39** was found to undergo thermal rearrangement back to the six-ring carbene **38**. There was no indication of any of the rearranged indenone-substituted carbene **40**. This result suggests that the highly strained cyclopropene **39** is thermodynamically less stable than the corresponding carbene **38** and that carbene **40** is also less stable than **38**. We suspect that this is also the case with the corresponding rhodium carbenoids. To further probe this point, we have carried out MO calculations using the semiempirical MNDO program. Calculations were performed with the standard version of MNDO as implemented in the MOPAC package which includes the PM3 parameters. Determination of the calculated heats of formation indicate that carbene **40** is the highest energy species ($R_1 = R_2 = H$) in this series of intermediates. The calculations clearly indicate that thermodynamic factors are not particularly important in influencing the 5-*exo* vs 6-*endo* cyclization selectivity of the *o*-alkynyl-substituted α-diazoacetophenone system. Rather, the regioselectivity of cyclization seems to be highly dependent on the nature of the substituent attached to the alkyne tether.[53] We suggest that the 5-*exo* vs 6-*endo* selectivity is due to steric interactions between the substituent on the alkyne and the ligand groups on the catalyst. When a terminal alkyne is used (i.e., **41**; R = H), only products derived from 6-*endo* closure are observed. On the other hand, alkynyl-substituted α-diazo ketones (i.e., **41**; R = alkyl) lead to products derived from 5-*exo* cyclization. In addition, the ability of the substituent group to stabilize the cyclic vinylogous carbenoid **43** also appears to be an important factor.





We have also carried out a number of experiments designed to probe the transient existence of a strained cyclopropene in these systems. It is not at all clear whether a cyclopropene intermediate (i.e., **19**, Scheme II) is involved in any of the cyclization chemistry. Cyclopropenes are known to readily undergo rhodium(II)-catalyzed ring opening to produce species such as **18** or **3**,[54] and this complicates the mechanistic interpretation. The interception of highly strained and reactive cyclopropenes with furan by a Diels–Alder reaction is well established.[55–57] Consequently, we decided to carry out the Rh(II)-catalyzed reaction of a typical *o*-alkynyl α-diazoacetophenone in the presence of furan with the hope of trapping an intermediate such as **19**.[58] Exposure of α-diazo ketone **44** to the rhodium(II) catalyst at 25 °C afforded the (*Z*)-keto aldehyde **45** in 91% yield. A similar reaction occurred using 2-methylfuran as the trapping agent which gave **46** in 94% yield. No signs of the [4 + 2]-cycloadduct **50** derived from cyclopropene **49** could be found in the crude reaction mixture. The formation of **45** is consistent with bimolecular cyclopropanation of **47** to give **48** which then undergoes the well-known [4 + 2]-cycloreversion reaction to produce **45**.[59–62]



We also attempted to trap a cyclopropene intermediate by incorporating a furan ring on the alkynyl side chain.

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(52) Bucher, G.; Sander, W. *J. Org. Chem.* **1992**, *57*, 1346.

(53) A similar conclusion was reached by Hoye and Dinsmore.[37d]

(54) Müller, P.; Pautex, N.; Doyle, M. P.; Bagheri, V. *Helv. Chim. Acta* **1990**, *73*, 1233.

(55) Billups, W. E.; Haley, M. M.; Lee, G. A. *Chem. Rev.* **1989**, *89*, 1147.

(56) Chenier, P. J.; Southland, D. A. *J. Org. Chem.* **1989**, *54*, 3519.

(57) Halton, B.; Bridle, J. H.; Lovett, E. G. *Tetrahedron Lett.* **1990**, 1313.

(58) Bicyclo[3.1.0]hex-1(6)-ene has yet to be detected and the number of recorded derivatives are few;[57] see: Baird, M. S.; Nethercott, W. *Tetrahedron Lett.* **1983**, *24*, 605. Coleman, B.; Jones, M., Jr. *J. Organomet. Chem.* **1979**, *168*, 393.

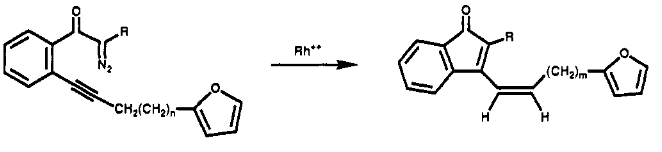
(59) Adams, J.; Rokach, J. *Tetrahedron Lett.* **1984**, *25*, 35. Rokach, J.; Adams, J.; Perry, R. *Tetrahedron Lett.* **1983**, *24*, 5185.

(60) Nwaji, M. N.; Onyiriuka, O. O. *Tetrahedron Lett.* **1974**, 2255.

(61) Padwa, A.; Wisnieff, T. J.; Walsh, E. J. *J. Org. Chem.* **1989**, *54*, 299.

(62) Wenkert, E.; Guo, M.; Pizzo, F.; Ramachandran, K. *Helv. Chim. Acta* **1987**, *70*, 1429.

The first compound investigated was α-diazo ketone **51**. Treatment of **51** with Rh(II) mandelate afforded only the 1,2-hydrogen shift product **52** in 65% yield. Since the possibility exists that the tether present in **51** was too short to allow for the parallel plane approach of π orbitals, we also examined the Rh(II)-catalyzed behavior of the homologous α-diazo ketone **53**. Once again, the only compound that was isolated corresponded to vinylindenone **54** (90%). Our failure to trap the putative cyclopropene indicates that either it is never formed or else is rapidly converted back to the rhodium carbenoid **47**.



51; R=H; n=2
53; R=Me; n=3

52; R=H; m=2
54; R=Me; m=3

In conclusion, the high efficiency of the intramolecular rhodium(II)-catalyzed cyclization reaction of *o*-alkynyl-substituted α-diazoacetophenones coupled with the simplicity of the procedure promises to provide an efficient route to a variety of substituted cycloalkenones. We are continuing to explore the scope and mechanistic details of these cyclization reactions and will report additional findings at a later date.

Experimental Section

Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70 eV. Unless otherwise noted, all reactions were performed in oven-dried glassware under an atmosphere of extra dry nitrogen. Solvents were evaporated under reduced pressure with a rotary evaporator, and the residue was chromatographed on a silica gel column using an ethyl acetate–hexane mixture as the eluent unless specified otherwise. Approximately 5 mg of catalyst was used to decompose 0.001 mmol of the α-diazo ketone.

Preparation and Rhodium(II)-Catalyzed Rearrangement of 2-(3-Methyl-1-butynyl)-α-diazoacetophenone (4). To a solution containing 5.24 g of methyl 2-iodobenzoate and 2.72 g of 3-methyl-1-butyne in 50 mL of triethylamine was added 60 mg of dichlorobis(triphenylphosphine)palladium(II) and 60 mg of CuI under Ar. The reaction mixture was heated at 60 °C for 1 h. After cooling, the mixture was filtered and concentrated under reduced pressure. Chromatography of the resulting brown oil on silica gel gave 3.84 g (95%) of methyl 2-(3-methyl-1-butynyl)benzoate: IR (neat) 1735, 1660, 1450, 1255, and 760 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.30 (d, 6 H, *J* = 6.0 Hz), 2.86 (sept, 1 H, *J* = 6.0 Hz), 3.93 (s, 3 H), 7.20–7.55 (m, 3 H), and 7.80–7.95 (m, 1 H).

To a stirred solution containing 2.57 g of potassium trimethylsilanolate[63] in 150 mL of ether was added 4.05 g of the above ester. The reaction mixture was stirred for 5 h at rt under N_2. After the mixture was cooled to 0 °C, 3.78 g of methyl chloroformate was added, and the reaction mixture was stirred for an additional 3 h at 25 °C. The solution was filtered, an ethereal diazomethane solution (75 mmol) was added, and the mixture was stirred for 16 h. The excess diazomethane and ether were removed under reduced pressure, and the resulting residue was chromatographed on silica gel. The major fraction contained 2.79 g (66%) of 2-(3-methyl-1-butynyl)-α-diazoacetophenone (**4**): IR (neat) 2250, 2150, 1640, 1360, 1030, and 770 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.26 (d, 6 H, *J* = 6.2 Hz), 2.83 (sept, 1 H, *J* = 6.2 Hz), 6.25 (bs, 1 H), 7.20–7.50 (m, 3 H), and 7.60–7.80 (m, 1 H).

A solution containing 250 mg of **4** in 20 mL of anhydrous benzene was treated with a catalytic amount of rhodium(II) mandelate under N_2. After the solution was stirred for 24 h at rt, the solvent was removed under reduced pressure. Chromatography of the resulting brown residue on a silica gel column afforded 210 mg (97%) of 3-(2-methyl-1-propenyl)-inden-1-one (**6**): mp 78–79 °C; IR (CH_2Cl_2) 1700, 1630, 1555, 1210, 1090, and 860 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.00 (s, 3 H), 2.05 (s, 3 H), 5.76 (s, 1 H), 6.16 (bs, 1 H), and 7.20–7.50 (m, 4 H). Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.79; H, 6.50.

Preparation and Rhodium-Catalyzed Behavior of 2-(2-Methoxy-2-methyl-3-butyn-4-yl)-α-diazoacetophenone (7). To a solution containing 10.75 g of methyl 2-bromobenzoate and 5.04 g of 2-methyl-3-butyn-2-ol in 150 mL of triethylamine was added 50 mg of dichlorobis(triphenylphosphine)palladium(II), 50 mg of CuI, and 100 mg of triphenylphosphine under Ar. The reaction mixture was heated at reflux for 10 h. After cooling, the mixture was filtered and concentrated under reduced pressure. The resulting brown oil was distilled under reduced pressure (bp 134 °C (0.5 mm)) to give 10.37 g (95%) of methyl 2-(2-hydroxy-2-methyl-3-butyn-4-yl)benzoate: IR (neat) 1730, 1610, 1310, 1260, and 780 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.40 (s, 6 H), 3.85 (s, 1 H), 7.25–7.70 (m, 3 H), and 7.80–7.95 (m, 1 H).

To a solution containing 6.69 g of the above material in 100 mL of toluene was added 1.24 g of NaH (60% dispersion) at 25 °C. After the mixture was stirred for 20 min, 4.2 g of CH_3I was added dropwise, and the reaction mixture was stirred for an additional 16 h. The mixture was filtered, and the solvent was removed under reduce pressure. Chromatography of the residue on silica gel afforded 5.0 g (70%) of methyl 2-(2-methoxy-2-methyl-3-butyn-4-yl)benzoate: IR (neat) 1745, 1635, 1375, 1270, 1090, and 780 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.45 (s, 6 H), 3.45 (s, 3 H), 3.85 (s, 3 H), 7.25–7.60 (m, 4 H), and 7.85–7.95 (m, 1 H).

A 2.66-g sample of the above ester was treated with 1.47 g of potassium trimethylsilanolane in 75 mL of ether, then with 1.6 mL of methyl chloroformate, and then with 40 mmol of a diazomethane in ether solution to give 2.07 g (75%) of 2-(3-methyl-1-butynyl)-α-diazoacetophenone (**7**): IR (neat) 2120, 1635, 1600, 1375, 1040, and 780 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.56 (s, 6 H), 3.46 (s, 3 H), 6.10 (s, 1 H), 7.40 (m, 3 H), and 7.81–7.95 (m, 1 H).

A solution containing 2.08 g of **7** in 30 mL of anhydrous benzene was treated with a catalytic amount of rhodium(II) mandelate under N_2. After the mixture was stirred for 30 min at rt, the solvent was removed under reduced pressure, and the residue was chromatographed on a silica gel column to give 900 mg (49%) of (*E*)-3-(2-methoxy-1-methyl-1-propen-1-yl)inden-1-one (**8a**): IR (neat) 1705, 1645, 1210, 1085, 1045, and 760 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.91 (s, 3 H), 1.97 (s, 3 H), 3.70 (s, 3 H), 5.59 (s, 1 H), 7.06–7.42 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.1, 20.6, 58.4, 112.0, 12.8, 126.2, 126.8, 129.0, 131.3, 133.6, 144.1, 144.5, 146.6, and 197.5; UV (95% ethanol) 242 (ε 23 300) and 324 nm (ε 4100); HRMS calcd for $C_{14}H_{14}O_2$ 214.0994, found 214.0991.

The minor fraction contained 608 mg (33%) of (*Z*)-3-(2-methoxy-1-methyl-1-propen-1-yl)inden-1-one (**8b**): mp 63–64 °C; IR (neat) 1705, 1645, 1640, 1395, 1290, and 1045 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.92 (s, 3 H), 1.97 (s, 3 H), 3.69 (s, 3 H), 5.59 (s, 1 H), and 7.06–7.41 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.1, 20.7, 29.7, 58.5, 122.1, 122.9, 126.3, 126.8, 129.1, 131.3, 133.6, 144.1, 144.6, 156.7, and 197.5; UV (95% ethanol) 242 (ε 23 300) and 324 nm (ε 4100); HRMS calcd for $C_{14}H_{14}O_2$ 214.0994, found 214.0992.

Preparation and Rhodium(II)-Catalyzed Behavior of 2-(2-Hydroxy-2-methyl-3-butyn-4-yl)-α-diazoacetophenone (10). To a stirred solution containing 0.7 g of potassium trimethylsilanolate in 30 mL of dry ether was added 1.0 g of methyl 2-(2-hydroxy-2-methyl-3-butyn-4-yl)benzoate. The reaction was stirred for 2 h at rt under N_2, 1.16 mL of methyl chloroformate was added dropwise, and the reaction was stirred for an additional 2 h at 25 °C. The solution was filtered, an ethereal diazomethane solution (20 mmol) was added, and the mixture was stirred for 2 h. The excess diazomethane and ether were removed under reduced pressure, and the resulting residue was chromatographed on silica gel to give 510 mg (52%) of 2-(2-hydroxy-2-methyl-3-butyn-4-yl)-α-diazoacetophenone (**10**): IR (neat) 2210, 2110, 1620, 1375, and 1170 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.63 (s, 6 H), 3.72 (s, 1 H), 6.20 (s, 1 H), 7.25–7.50 (m, 2 H), and 7.60–7.80 (m, 2 H).

To a solution containing 300 mg of **10** in 15 mL of anhydrous dichloromethane was added a catalytic amount of rhodium(II) mandelate. After the mixture was stirred for 30 min at rt, the solvent was removed under reduced pressure, and the mixture was chromatographed on silica gel to give 218 mg (83%) of 3-

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[63] Laganis, E. D.; Chenard, B. L. *Tetrahedron Lett.* **1984**, *25*, 5831.

[2-(3-oxobutylidene)]-1*H*-indanone (**9**): mp 124–125 °C; IR (KBr) 1715, 1685, 1270, 1240, 780, and 760 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.39 (s, 3 H), 2.44 (s, 3 H), 3.57 (s, 2 H), 7.51–7.72 (m, 2 H), 7.86 (d, 1 H, J = 7.8 Hz), and 7.95 (d, 1 H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.5, 28.7, 44.0, 122.6, 127.0, 130.1, 131.2, 133.2, 138.2, 139.1, 148.0, 202.3, and 202.9. Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.90; H, 6.03. Found: C, 77.70; H, 6.10.

Preparation and Rhodium(II)-Catalyzed Behavior of 2-[2-(1-Hydroxycyclopentyl)ethynyl]-*α*-diazoacetophenone (11). To a solution containing 5.42 g of methyl 2-bromobenzoate and 2.5 g of 1-ethynylcyclopentanol in 50 mL of triethylamine was added 50 mg of dichlorobis(triphenylphosphine)palladium(II), 100 mg of triphenylphosphine, and 50 mg of CuI under Ar. The reaction mixture was heated at reflux for 16 h. After cooling, the mixture was filtered and concentrated under reduced pressure. The resulting brown oil was chromatographed on silica gel to give 4.7 g (87%) of methyl 2-[2-(1-hydroxycyclopentyl)ethynyl]benzoate: IR (neat) 2220, 1735, 1300, 1255, and 780 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 1.80–2.20 (m, 8 H), 3.16 (s, 1 H), 3.95 (s, 3 H), 7.38–7.63 (m, 3 H), and 7.85–8.15 (m, 1 H).

To a stirred solution containing 1.44 g of potassium trimethylsilanolate in 50 mL of ether was added 2.50 g of the above material. After the mixture was stirred under N_2 at rt for 4 h, 2.32 mL of methyl chloroformate was added, and the reaction mixture was stirred for an additional 2 h. After filtration, an ethereal diazomethane solution (40 mmol) was added, and the mixture was stirred for 3 h. The excess diazomethane was removed under reduced pressure, and the residue was chromatographed on silica gel to give 1.36 g (55%) of 2-[2-(1-hydroxycyclopentyl)ethynyl]-*α*-diazoacetophenone (**11**): IR (neat) 2120, 1640, 1375, 1020, and 760 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.80–2.15 (m, 8 H), 3.28 (s, 1 H), 6.21 (s, 1 H), 7.25–7.55 (m, 3 H), and 7.60–7.80 (m, 1 H).

A solution containing 250 mg of **11** in 50 mL of anhydrous CH_2Cl_2 was treated with a catalytic amount of rhodium(II) octanoate. After the mixture was stirred for 15 min at 25 °C, the solvent was removed under reduced pressure, and the residue was chromatographed on silica gel to give 175 mg (82%) of 3-(2-oxo-1-cyclohexylidene)-1*H*-indan-1-one (**13**) as a 1:1 mixture of stereoisomers. Fractional crystallization afforded one of the stereoisomers as a white solid: mp 130–131 °C; IR (KBr) 1710, 1675, 1275, 1250, 1150, and 780 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.87–1.92 (m, 4 H), 2.51 (t, 2 H, J = 6.3 Hz), 3.08 (t, 2 H, J = 5.7 Hz), 3.66 (s, 2 H), 7.49–7.54 (m, 1 H), 7.65–7.71 (m, 1 H), and 7.85–7.93 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.3, 23.1, 30.4, 41.0, 44.4, 123.1, 127.4, 129.5, 131.9, 133.9, 138.6, 139.5, 148.1, 202.1, and 202.9. Anal. Calcd for $C_{15}H_{14}O_2$: C, 78.57; H, 6.57. Found: C, 78.52; H, 6.26.

Preparation and Rhodium(II)-Catalyzed Behavior of 2-[2-(1-Hydroxycyclohexyl)ethynyl]-*α*-diazoacetophenone (12). To a solution containing 4.67 g of methyl 2-bromobenzoate and 3.0 g of 1-ethynylcyclohexanol in 50 mL of triethylamine was added 50 mg of dichlorobis(triphenylphosphine)palladium(II), 100 mg of triphenylphosphine, and 50 mg of CuI under Ar. The reaction mixture was heated at reflux for 15 h. After cooling, the mixture was filtered and concentrated under reduced pressure, and the resulting brown oil was chromatographed on silica gel to give 4.76 g (86%) of methyl 2-[2-(1-hydroxycyclohexyl)ethynyl]benzoate: IR (neat) 1720, 1294, 1254, and 780 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 1.19–1.69 (m, 10 H), 3.32 (s, 1 H), 3.85 (s, 3 H), and 7.24–7.63 (m, 4 H).

To a stirred solution containing 1.24 g of potassium trimethylsilanolate in 50 mL of ether was added 2.50 g of the above material. After the mixture was stirred under N_2 at rt for 4 h, 1.55 mL of methyl chloroformate was added, and the mixture was stirred for an additional 2 h at rt. After filtration, an ethereal diazomethane solution (20 mmol) was added, and the solution was stirred for 3 h. The excess diazomethane was removed under reduced pressure, and the residue was chromatographed on silica gel to give 1.36 g (56%) of 2-[2-(1-hydroxycyclohexyl)ethynyl]-*α*-diazoacetophenone (**12**): IR (neat) 1635, 1365, 965, and 750 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.20–1.69 (m, 10 H), 3.37 (s, 1 H), 6.22 (s, 1 H), and 7.24–7.63 (m, 4 H).

A solution containing 250 mg of **12** in 50 mL of anhydrous CH_2Cl_2 was treated with a catalytic amount of rhodium(II) octanoate. After the mixture was stirred for 15 min at rt, the solvent was removed under reduced pressure, and the residue was chromatographed on silica gel to give 237 mg (83%) of a 1:1 cis/trans mixture of 3-(2-oxo-1-cycloheptylidene)-1*H*-indan-1-one (**14**): IR (neat) 1715, 1685, 1600, 1255, 945, and 785 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.85–2.05 (m, 12 H), 2.42 (m, 2 H), 2.60 (m, 4 H), 2.88 (m, 2 H), 3.20 (s, 2 H), 3.50 (s, 2 H), 7.3–7.8 (m, 8 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.5, 23.7, 27.0, 27.5, 28.8, 28.9, 29.9, 30.9, 40.1, 42.1, 42.4, 43.0, 122.9, 123.2, 124.0, 125.8, 128.6, 129.1, 129.8, 134.0, 134.2, 134.3, 137.3, 137.5, 137.6, 139.3, 146.6, 147.7, 200.5, 202.5, 206.8, and 210.2; HRMS calcd for $C_{16}H_{16}O_2$ 240.1150, found 240.1147.

Preparation of 2-(1-Heptynyl)-*α*-diazoacetophenone (15). To a deareated solution containing 14.0 g of methyl 2-iodobenzoate and 5.77 g of 1-heptyne in 300 mL of triethylamine was added 140 mg of dichlorobis(triphenylphosphine)palladium(II) and 140 mg of cuprous iodide under Ar. The reaction mixture was heated at 50 °C for 1 h. After cooling, the mixture was filtered and concentrated under reduced pressure. Chromatography of the resulting brown oil on silica gel gave 11.56 g (94%) of methyl 2-(1-heptynyl)benzoate: IR (neat) 1750, 1305, 1260, 1095, and 720 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.05 (t, 3 H, J = 6.0 Hz), 1.20–1.90 (m, 6 H), 2.24 (t, 2 H, J = 6.0 Hz), 3.95 (s, 3 H), 7.20–7.65 (m, 3 H), and 7.85–8.00 (m, 1 H).

A solution containing 2.24 g of the above material, 1.36 g of potassium hydroxide, 33 mL of water, and 100 mL of methanol was heated for 3 h. After cooling, the mixture was concentrated under reduced pressure, the resulting solution was brought to pH 4 with a 10% aqueous solution of HCl, and the mixture was extracted with 100 mL of ether. The ether layer was dried over sodium sulfate and was then stirred for 30 min with 4.0 g of triethylamine. The mixture was cooled to 0 °C, treated with 2.32 mL of methyl chloroformate, slowly brought to rt, and stirred for 12 h. The solution was filtered, an ethereal solution of diazomethane (75 mmol) was added to the filtrate, and the mixture was stirred for 12 h at rt. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel. The major fraction contained 1.17 g (50%) of 2-(1-heptynyl)-*α*-diazoacetophenone (**15**): IR (neat) 2260, 2110, 1630, 1360, 880, and 770 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.89 (t, 3 H, J = 7.0 Hz), 1.27–1.48 (m, 4 H), 1.60 (q, 1 H, J = 7.0 Hz), 2.43 (t, 2 H, J = 7.0 Hz), 6.31 (bs, 1 H), and 7.20–7.75 (m, 4 H).

A solution containing 100 mg of **15** in 50 mL of $CHCl_3$ was treated with a catalytic amount of rhodium(II) mandelate under N_2. After the mixture was stirred for 30 min at rt, the solvent was removed under reduced pressure, and the resulting bright yellow residue was chromatographed on a silica gel column. The major fraction contained 82 mg of an oil (82%) which was identified as a 1:1 mixture of the C–H insertion product 3-(2-methyl-1-cyclopentyl)inden-1-one (**16**) (1:2 parts cis/trans) and the 1,2-hydrogen shift product, (*Z*)-3-(1-hexenyl)inden-1-one (**17**) on the basis of the spectral properties of the mixture. Repeated chromatographic separations eventually afforded a sample of the *E* isomer of **16**: IR (CH_2Cl_2) 1710, 1145, 1090, 1020, and 815 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.04 (d, 3 H, J = 6.5 Hz), 1.35 (m, 1 H), 1.60–1.90 (m, 3 H), 1.93–2.05 (m, 1 H), 2.08–2.23 (m, 2 H), 2.55 (dd, 1 H, J = 17.1, and 8.5 Hz), 5.65 (s, 1 H), and 7.10–7.53 (m, 4 H). Anal. Calcd for $C_{15}H_{16}O$: C, 84.86; H, 7.60. Found: C, 84.79; H, 7.53. The spectral data for the *Z*-isomer of **16** was obtained by substraction from the cis/trans mixture: Compound *Z*-**16**: NMR ($CDCl_3$, 300 MHz) δ 0.75 (d, 3 H, J = 7.1 Hz), 0.80–2.25 (m, 7 H), 3.03 (m, 1 H), 5.66 (s, 1 H), and 7.10–7.53 (m, 4 H).

A pure sample of *Z*-olefin **17** was obtained by extensive chromatographic separations: IR ($CHCl_3$) 1700, 1603, 1457, 1193, 1082, and 879 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 0.90 (t, 3 H, J = 7.2 Hz), 1.25–1.50 (m, 4 H), 2.38 (dt, 2 H, J = 7.1 and 6.8 Hz), 5.83 (s, 1 H), 6.24 (dt, 1 H, J = 12.0 and 6.8 Hz), 6.32 (d, 1 H, J = 12.0 Hz), and 7.10–7.53 (m, 4 H). Anal. Calcd for $C_{15}H_{16}O$: C, 84.86; H, 7.60. Found: C, 84.62; H, 7.45.

Preparation and Rhodium-Catalyzed Reaction of *o*-(5-(Allyloxy)-1-pentynyl)-*α*-diazoacetophenone (24). To a solution containing 2.0 g (10 mmol) of 4-pentyn-1-ol in 35 mL of THF was added 0.95 g of NaH (60% dispersion). The mixture was stirred under N_2 for 30 min at 0 °C, and then 3.67 g (1.2 equiv) of allyl bromide was added dropwise. Stirring was continued overnight at rt, the mixture was filtered, and the solvent was removed under reduced pressure. The crude residue was distilled at 45 °C (0.5 mm) to give 1.85 g (63%) of 5-(allyloxy)-1-pentyne: IR (neat) 2125, 1450, 1360, 1200, 1010, and 920 cm^{-1}; NMR (300 MHz, CDCl$_3$) δ 1.80 (q, 2 H, J = 6.5 Hz), 1.91 (m, 2 H), 2.26 (m, 2 H), 3.49 (t, 2 H, J = 6.5 Hz), 3.95 (d, 1 H, J = 5.7 Hz), 5.12 (d, 1 H, J = 10.5 Hz), 5.24 (d, 1 H, J = 15.6 Hz), and 5.85 (ddt, 1 H, J = 15.6, 10.5, and 5.7 Hz).

To a solution containing 1.2 g (4.6 mmol) of methyl 2-iodobenzoate in 25 mL of dry triethylamine was added 0.7 g (6.0 mmol) of 5-(allyloxy)-1-pentye. The solution was stirred at 80 °C under Ar for 20 min before adding 0.05 g of dichlorobis(triphenylphosphine)palladium(II), 0.05 g of CuI, and 0.1 g of triphenylphosphine. The reaction mixture was heated at reflux for 6 h, cooled, and filtered, and the solvent was removed under pressure. The crude residue was chromatographed on silica gel. The major fraction contained 1.0 g (84%) of methyl *o*-(5-(allyloxy)-1-pentynyl)benzoate; IR (neat) 3090, 2215, 1725, 1610, 1445, 1370, and 1090 cm^{-1}; NMR (CDCl$_3$, 300 MHz) δ 1.87 (q, 2 H, J = 6.9 Hz), 2.54 (t, 2 H, J = 6.9 Hz), 3.57 (t, 2 H, J = 6.9 Hz), 3.86 (s, 3 H), 3.91 (d, 2 H, J = 5.4 Hz), 5.12 (d, 1 H, J = 10.7 Hz), 5.24 (d, 1 H, J = 16.0 Hz), 5.87 (ddt, 1 H, J = 16.0, 10.7, and 5.4 Hz), and 7.23–7.82 (m, 4 H).

A 850-mg sample of the above ester was added in one portion to a stirred solution containing 500 mg of potassium trimethylsilanolate in 30 mL of ether at room temperature under N$_2$. The reaction mixture was stirred for 3 h, and then 10 mmol of methyl chloroformate was added dropwise. The solution was stirred for an additional 2 h, and the solid that formed was collected by filtration. To the resulting solution was added 20 mmol of diazomethane, and the mixture was stirred for an additional 2 h at rt. The solvent was removed under reduced pressure, and the crude residue was chromatographed on a silica gel column to give 520 mg (60%) of *o*-(5-(allyloxy)-1-pentynyl)-α-diazoacetophenone (**24**): IR (neat) 1630, 1495, 1370, and 1120 cm^{-1}; NMR (CDCl$_3$, 300 MHz) δ 1.87 (q, 2 H, J = 6.6 Hz), 2.55 (t, 2 H, J = 6.9 Hz), 3.57 (t, 2 H, J = 6.6 Hz), 3.95 (d, 2 H, J = 5.4 Hz), 5.16 (d, 1 H, J = 10.0 Hz), 5.28 (d, 1 H, J = 16.2 Hz), 5.90 (ddt, 1 H, J = 16.2, 10.0, and 5.4 Hz), 6.28 (s, 1 H), and 7.24–7.67 (m, 4 H).

A solution containing 200 mg of **24** in 15 mL of dry CH$_2$Cl$_2$ was treated with 5 mg of Rh(II) mandelate. The reaction mixture was stirred at rt for 30 min. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel column. The only fraction that was isolated contained 145 mg (81%) of 2-(2-propen-1-yl)-2-(1-oxo-1*H*-indenyl)-2,3,4,5-tetrahydrofuran (**27**): IR (neat) 1715, 1610, 1460, 1200, and 1060 cm^{-1}; NMR (CDCl$_3$, 300 MHz) δ 1.90–2.20 (m, 4 H), 2.63 (m, 2 H), 3.85 (m, 1 H), 3.95 (m, 1 H), 5.05 (m, 2 H), 5.35 (m, 1 H), 5.75 (s, 1 H), and 7.10–7.40 (m, 4 H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 25.2, 34.0, 42.6, 67.4, 83.9, 117.9, 121.6, 121.7, 128.3, 131.9, 132.3, 132.4, 132.6, 142.5, 168.8, and 196.7; HRMS calcd for $C_{16}H_{16}O_2$ 240.1150, found 240.1148.

Preparation and Rhodium(II)-Catalyzed Behavior of 2-Ethynyl-α-diazoacetophenone (28). To a solution containing 2.0 g of methyl 2-(3-methyl-3-hydroxy-1-butynyl)benzoate in 50 mL of toluene was added 80 mg of NaH (60% dispersion). The stirred suspension was slowly distilled until the boiling point of the distillate reached 110 °C. The solution was cooled, filtered, and concentrated under reduced pressure. The resulting oil was dissolved in CH$_2$Cl$_2$ and was washed with a 10% aqueous NaHCO$_3$ solution and water. After being dried over MgSO$_4$, the solution was concentrated under reduced pressure, and the residue was chromatographed to give 1.20 g (65%) of methyl 2-ethynylbenzoate:[64] IR (neat) 1725, 1460, 1235, and 1105 cm^{-1}; NMR (CDCl$_3$, 90 MHz) δ 3.45 (s, 1 H), 3.95 (s, 3 H), 7.40–7.70 (m, 3 H), and 7.80–7.95 (m, 1 H).

To a stirred solution containing 0.96 g of potassium trimethylsilanolate in 50 mL of ether was added 1.22 g of the above ester. The reaction mixture was stirred for 5 h at rt under N$_2$. After the mixture was cooled to 0 °C, 1.55 mL of methyl chloroformate was added, and the reaction mixture was stirred for an additional 3 h at 25 °C. After filtration, an ethereal diazomethane solution (30 mmol) was added, and the mixture was stirred for 16 h at rt. The excess diazomethane was removed under reduced pressure, and the resulting residue was chromatographed on silica gel to give 950 mg (75%) of 2-ethynyl-α-diazoacetophenone (**28**): IR (neat) 2170, 2115, 1635, 1380, 890, and 770 cm^{-1}; NMR (CDCl$_3$, 90 MHz) δ 3.38 (s, 1 H), 6.28 (s, 1 H), and 7.40–7.85 (m, 4 H).

A solution containing 500 mg of **28** in 35 mL of anhydrous methanol was treated with a catalytic amount of rhodium(II) mandelate. After heating at 80 °C for 1 h, the solvent was removed under reduced pressure. Chromatography of the residue on silica gel gave 280 mg (55%) of 4-methoxy-1-naphthol (**29**): mp 128–129 °C; IR (KBr) 3240, 3040, 2980, 1610, 1365, 1320, 1095, 775, and 740 cm^{-1}; NMR (CDCl$_3$, 300 MHz) δ 3.94 (s, 3 H), 4.85 (s, 1 H), 6.61 (d, 1 H, J = 8.1 Hz), 6.71 (d, 1 H, J = 8.1 Hz), 7.50 (m, 2 H), 8.09 (m, 1 H), and 8.19 (m, 1 H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 55.2, 102.8, 107.3, 120.7, 121.3, 124.6, 125.3, 125.7, 125.8, 144.3, and 149.2. Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.72; H, 5.85.

A 500-mg sample of **28** was heated in 2-propanol in the presence of a catalytic amount of rhodium(II) mandelate. The major product contained 238 mg (40%) of 4-isopropoxy-1-naphthol (**30**): mp 91–92 °C; IR (KBr) 1515, 1435, 1420, and 1215 cm^{-1}; NMR (CDCl$_3$, 300 MHz) δ 1.39 (d, 6 H, J = 6.0 Hz), 4.59 (sept., 1 H, J = 6.0 Hz), 4.89 (s, 1 H), 6.69 (d, 1 H, J = 8.4 Hz), 6.72 (d, 1 H, J = 8.4 Hz), 7.49 (m, 2 H), 8.20 (m, 1 H), and 8.22 (m, 1 H). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.19; H, 6.98. Found: C, 77.00; H, 6.93.

A solution containing 150 mg of **28** in 15 mL of anhydrous benzene was treated with a catalytic amount of rhodium(II) mandelate. After stirring for 6 h at rt, the solvent was removed under reduced pressure. Chromatography of the residue on silica gel afforded 94 mg (50%) of 4-phenyl-1-naphthol (**31**): mp 136–137 °C; IR (CHCl$_3$) 1590, 1355, 1245, 1050, and 770 cm^{-1}; NMR (CDCl$_3$, 300 MHz) δ 5.31 (s, 1 H), 6.85 (d, 1 H, J = 7.8 Hz), 7.23 (d, 1 H, J = 7.8 Hz), 7.45 (s, 5 H), 7.38–7.52 (m, 2 H), 7.85 (d, 1 H, J = 8.1 Hz), and 8.23 (d, 1 H, J = 8.1 Hz). Anal. Calcd for $C_{16}H_{12}O$: C, 87.25; H, 5.49. Found: C, 87.09; H, 5.21.

Preparation and Rhodium-Catalyzed Behavior of 3-Carbomethoxy-2-ethynyl-α-diazoacetophenone (32). A mixture containing 32.0 g of 2-bromo-*m*-xylene and 40.0 g of KMnO$_4$ in 600 mL of water was brought to reflux. After the mixture was heated for 24 h, a second portion of 40.0 g of KMnO$_4$ in 100 mL of water was added followed by a third portion 24 h later. The hot mixture was filtered over Celite, and the solid was washed twice with hot water. The solution was concentrated and cooled in an ice bath. Acidification using a 20% aqueous HCl solution precipitated the diacid which was filtered and dried over P$_2$O$_5$ to give 29.0 g (68%) of 2-bromoisophthalic acid:[65] mp 213–214 °C; IR (KBr) 2800, 1700, 1580, 1400, 1300, 1250, 960, and 760 cm^{-1}; NMR (CDCl$_3$, 90 MHz) δ 7.47 (t, 1 H, J = 7.5 Hz) and 7.64 (d, 2 H, J = 7.5 Hz).

To a solution containing 29.0 g of the above acid in 1.2 L of methanol was added 120 mL of concentrated aqueous sulfuric acid solution. The mixture was heated at reflux for 12 h and then concentrated to half of its original volume. Water and solid K$_2$CO$_3$ were added until the solution was at neutral pH. The aqueous mixture was extracted with ether, and the organic layer was dried over MgSO$_4$. Removal of the solvent under reduced pressure and distillation of the residue (bp 120–122 °C (0.9 mm)) afforded 27.0 g (84%) of methyl 2-bromoisophthalate: IR (KBr) 1730, 1590, 1430, 1260, 1210, 1160, and 1000 cm^{-1}; NMR (CDCl$_3$, 90 MHz) δ 3.95 (s, 6 H), 7.45 (m, 1 H), and 7.70 (d, 2 H, J = 7.5 Hz).

To a solution containing 6.9 g of the above diester and 7.5 mL of ethynyltrimethylsilane in 5 mL of triethylamine was added 130 mg of triphenylphosphine, 130 mg of CuI, and 70 mg of dichlorobis(triphenylphosphine)palladium(II). After being heated at reflux for 12 h, the mixture was cooled and filtered, and the solvent was removed under reduced pressure. The residue was dissolved in 100 mL of methanol which contained 500 mg of K$_2$CO$_3$. The solution was stirred for 5 h under N$_2$, and the solvent was removed under reduced pressure to give 2.9 g (53%) of methyl 2-ethynylisophthalate:[66] IR (CCl$_4$) 3260, 3020, 2960, 2110, 1730, 1260, 1000, and 760 cm^{-1}; NMR (CDCl$_3$, 90 MHz) δ 3.66 (s, 1 H),

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(64) Haves, S. J.; Hergenrother, P. M. *J. Org. Chem.* **1985**, *50*, 1763.

(65) James, C. W.; Kenner, J.; Stubbings, W. V. *J. Chem. Soc.* **1920**, 117.

(66) Austin, W. B.; Bilow, N.; Kelleghan, W. J.; Lau, K. S. Y. *J. Org. Chem.* **1981**, *46*, 2280.

4.00 (s, 6 H), 7.45 (t, 1 H, J = 7.5 Hz), and 7.95 (d, 2 H, J = 7.5 Hz); MS m/e (M + H) 219.

A solution containing 280 mg of the above diester and 280 mg of KOH in 5 mL of methanol was stirred at rt for 36 h. The mixture was concentrated, and 10 mL of water was added. The solution was extracted with ether, and the aqueous layer was acidified with a 10% aqueous HCl solution. The aqueous layer was extracted once more with ether and dried over $MgSO_4$. After the solution was cooled to 0 °C, 0.20 mL of methyl chloroformate in 2 mL of ether was added dropwise, and the mixture was stirred for 16 h at 25 °C. After filtration an ethereal diazomethane solution (7.2 mmol) was added to the cold solution, and the mixture was stirred for 8 h at rt. The solution was concentrated under reduced pressure, and the residue was chromatographed on silica gel to give 62 mg (21%) of 3-carbomethoxy-2-ethynyl-α-diazoacetophenone (**32**): IR (neat) 1735, 1620, 1360, 1150, and 765 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.63 (s, 1 H), 3.88 (s, 3 H), 5.96 (bs, 1 H), 7.42 (t, 1 H, J = 7.8 Hz), 7.65 (d, 1 H, J = 7.2 Hz), and 7.88 (d, 1 H, J = 7.5 Hz).

To a solution containing 80 mg of **32** in 20 mL of methanol was added a catalytic amount of rhodium(II) acetate under N_2. After the mixture was stirred for 12 h, the solvent was removed under reduced pressure, and the residue was chromatographed on silica gel. The first fraction contained 35 mg (43%) of 6-hydroxy-2,2-dimethoxy-2*H*-naphtho[1,8-*bc*]furan (**36**): IR (neat) 1715, 1475, 1450, 1255, 1130, 870, and 770 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.41 (s, 6 H), 5.50 (s, 1 H), 6.59 (d, 1 H, J = 7.5 Hz), 6.74 (d, 1 H, J = 7.5 Hz), 7.50 (d, 1 H, J = 6.9 Hz), 7.59 (t, 1 H, J = 7.8 Hz), and 7.97 (d, 1 H, J = 8.1 Hz). Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.22; H, 5.21. Found: C, 66.94; H, 5.08.

The second fraction contained 30 mg (37%) of 5-carbomethoxy-4-methoxy-1-naphthol (**35**): IR (neat) 1710, 1620, 1475, 1260, 765, and 730 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.84 (s, 3 H), 3.45 (s, 3 H), 5.86 (s, 1 H), 6.61 (d, 1 H, J = 8.4 Hz), 6.68 (d, 1 H, J = 8.4 Hz), 7.41 (m, 2 H), and 8.16 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.1, 56.3, 105.8, 108.5, 121.7, 123.3, 124.6, 124.5, 125.2, 128.6, 145.3, 148.1, and 172.2. Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.22; H, 5.21. Found: C, 67.03; H, 5.14.

Reaction of (*o*-(2-Phenylethynyl)benzoyl)diazoethane (44) with Rhodium(II) Acetate and Furan. A solution containing 100 mg (0.4 mmol) of **44** in 25 mL of furan was treated with a catalytic of rhodium(II) acetate at 25 °C. The reaction mixture was stirred for 30 min at 25 °C, concentrated under reduced pressure, and chromatographed on a silica gel column. The major fraction contained 103 mg (91%) of 5-(2-methyl-1-oxoinden-3-yl)-5-phenyl-(*E*,*Z*)-2,4-pentadienal (**45**): IR (neat) 1720, 1701, 1600, and 1450 cm^{-1}; NMR ($CDCl_3$, 300 Mz) δ 1.69 (s, 3 H), 6.20 (d, 1 H, J = 11.1 Hz), 6.62 (d, 1 H, J = 6.9 Hz), 6.78 (t, 1 H, J = 11.1 Hz), 7.09–7.38 (m, 9 H), and 10.25 (d, 1 H, J = 11.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.0, 120.8, 122.6, 124.8, 127.9, 128.4, 129.0, 129.3, 130.6, 133.3, 134.1, 135.7, 141.9, 144.0, 145.2, 154.0, 190.1, and 198.3; HRMS calcd for $C_{21}H_{16}O_2$ 300.1150, found 300.1149.

The same reaction was carried out using 25 mL of 2-methylfuran as the solvent. The major product formed in 94% yield was identified as 5-(2-methyl-1-oxoinden-3-yl)-6-phenyl-(*E*,*Z*)-3,5-hexadien-2-one (**46**): IR (neat) 2855, 1715, 1690, and 1169 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.69 (s, 3 H), 2.27 (s, 3 H), 6.20 (d, 1 H, J = 11.2 Hz), 6.61 (d, 1 H, J = 6.9 Hz), 6.78 (t, 1 H, J = 11.2 Hz), 7.06–7.40 (m, 8 H), and 7.95 (d, 1 H, J = 11.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.0, 31.6, 121.0, 122.3, 126.8, 127.6, 128.7, 129.9, 130.8, 133.2, 136.3, 137.7, 145.5, 197.3, and 198.7; HRMS calcd for $C_{22}H_{18}O_2$ 314.1306, found 314.1216.

Preparation and Rhodium(II)-Catalyzed Reaction of *o*-(5-(2-Furyl)-1-pentynyl)-α-diazoacetophenone (51). To a solution containing 5.4 g of furan (80 mmol) in 30 mL of dry THF was added 85 mmol of *n*-BuLi dropwise at −10 °C under N_2. The reaction mixture was stirred for 30 min at −10 °C, and then 12.5 g (80 mmol) of 1-bromo-3-chloropropane was added dropwise. Stirring was continued for an additional 3 h at rt. The reaction mixture was washed with 100 mL of a saturated aqueous solution of NH_4Cl and extracted with ether. The ether layer was dried over magnesium sulfate and concentrated under reduced pressure. The crude residue was distilled at 45 °C (0.5 mm) to give 7.4 g (59% yield) of 1-chloro-3-furylpropane: IR (neat) 1605, 1515, 1300, 1250, and 1090 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.09 (q, 2 H, J = 7.0 Hz), 2.80 (t, 2 H, J = 7.0 Hz), 3.54 (t, 2 H, J = 7.0 Hz), 6.04 (d, 2 H, J = 2.1 Hz), 6.28 (m, 1 H) and 7.30 (d, 1 H, J = 2.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.0, 30.8, 43.9, 106.3, 110.0, 141.0, and 145.2.

A solution containing 4.3 g (65 mmol) of lithium acetylide–ethylenediamine complex in 50 mL of dry DMSO was warmed to 48 °C, and then 6.0 g (40 mmol) of 1-chloro-3-furylpropane was added dropwise at 48 °C over a period of 45 min. Once the addition was complete, the reaction mixture was stirred at 48 °C for 3 h, washed with water, and extracted with ether. The ether layer was washed with a saturated aqueous solution of NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was distilled at 52 °C (0.5 mm) to give 2.2 g (45%) of 5-(2-furyl)-1-pentyne: IR (neat) 3300, 2980, 2115, 1600, 1455, and 940 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.88 (q, 2 H, J = 7.2 Hz), 2.42 (m, 3 H), 2.80 (t, 2 H, J = 7.2 Hz), 6.05 (d, 1 H, J = 1.7 Hz), 6.27 (m, 1 H), and 7.29 (d, 1 H, J = 1.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.7, 26.7, 26.8, 68.7, 83.6, 105.1, 109.9, 140.8, and 154.9.

To a solution containing 2.5 g of methyl 2-iodobenzoate in 50 of dry triethylamine was added 2.0 g (15 mmol) of 5-(2-furyl)-1-pentyne. The mixture was stirred at 25 °C under Ar for 20 min, and then 0.05 g of CuI, 0.01 g of triphenylphosphine, and 0.05 g of dichlorobis(triphenylphosphine)palladium(II) were added. The reaction mixture was heated at reflux for 6 h, cooled, filtered, and concentrated under reduced pressure. The crude residue was chromatographed on a silica gel column to give 1.1 g (40% yield) of methyl *o*-(5-(2-furyl)-1-pentynyl)benzoate; IR (neat) 2970, 2220, 1725, 1595, 1450, and 1090 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.94 (q, 2 H, J = 7.2 Hz), 2.49 (t, 2 H, J = 7.2 Hz), 2.82 (t, 2 H, J = 7.2 Hz), 3.86 (s, 3 H), 6.03 (d, 1 H, J = 2.1 Hz), 6.12 (m, 1 H), 7.28 (d, 1 H, J = 2.1 Hz), and 7.36–7.87 (m, 4 H).

To a solution containing 0.52 g (4 mmol) of potassium trimethylsilanolate in 50 mL of anhydrous ether was added 1.0 g (3 mmol) of the above ester. The reaction mixture was stirred for 2 h at rt under N_2. After the mixture was cooled to 0 °C, 0.70 g (8 mmol) of methyl chloroformate was added, and the reaction mixture was stirred for an additional 2 h at 25 °C. The solution was filtered, an ethereal solution of diazomethane (25 mmol) was added, and stirring was continued for 4 h at 25 °C. Th excess ether and diazomethane were removed under reduced pressure, and the resulting residue was chromatographed on silica gel to give 0.62 g (60%) of *o*-(5-(2-furyl)-1-pentynyl)-α-diazoacetophenone (**51**): IR (neat) 2240, 2135, 1635, 1460, and 1040 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.93 (q, 2 H, J = 7.2 Hz), 2.48 (t, 2 H, J = 7.2 Hz), 2.79 (t, 2 H, J = 7.2 Hz), 6.05 (m, 1 H), 6.28 (s, 1 H), 7.28 (m, 1 H), and 7.35–7.64 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.7, 26.5, 26.6, 56.6, 79.4, 95.9, 105.0, 109.9, 120.9, 127.5, 130.5, 133.4, 138.9, 140.6, 154.6, and 189.5.

A solution containing 200 mg (0.7 mmol) of **51** in 20 mL of dry CH_2Cl_2 was treated with a catalytic amount of rhodium(II) mandelate. The reaction mixture was stirred at rt for 20 min, the solvent was removed under reduced pressure, and the residue was chromatographed on silica gel. The major fraction (65%) was identified as 3-(4-furylbuten-1-yl)indenone (**52**): IR (neat) 1715, 1595, 1465, and 990 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.73 (m, 2 H), 2.85 (m, 2 H), 5.80 (s, 1 H), 6.05 (d, 1 H, J = 2.1 Hz), 6.20 (m, 1 H), 6.23–6.42 (m, 3 H), 7.25–7.43 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 27.2, 28.5, 105.2, 108.8, 116.6, 120.5, 121.3, 125.3, 130.1, 131.2, 134.2, 137.8, 140.1, 145.0, 152.2, 154.3, and 198.0; HRMS calcd for $C_{17}H_{14}O_2$ 250.0994, found 250.0994.

Preparation and Reaction of (*o*-(6-(2-Furyl)-1-hexynyl)-benzoyl)diazoethane (53) with Rhodium(II) Octanoate. A mixture containing 3.0 g (11.5 mmol) of methyl *o*-iodobenzoate and 2.0 g of 6-(2-furyl)-1-hexyne was converted into 1.75 g (55%) of methyl-*o*-(6-(2-furyl)-1-hexynyl)benzoate under typical Castro–Stephens arylation conditions: IR (neat) 1732, 1433, 1294, and 1084 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.69 (m, 2 H), 1.83 (m, 2 H), 2.48 (t, 2 H, J = 6.9 Hz), 2.66 (t, 2 H, J = 6.9 Hz), 3.86 (s, 3 H), 5.99 (d, 1 H, J = 1.5 Hz), 6.25 (m, 1 H), 7.23 (d, 1 H, J = 1.5 Hz), and 7.25–7.84 (m, 4 H).

A 1.5-g (5.3-mmol) sample of the above ester was converted with diazoethane in the normal fashion into 0.65 g of (*o*-(5-(2-furyl)-1-hexynyl)benzoyl)diazoethane (**53**): IR (neat) 2073, 1616, 1340, and 980 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.58 (m, 2 H), 1.76 (m, 2 H), 2.02 (bs, 3 H), 2.42 (t, 2 H, J = 7.0 Hz), 2.65 (t, 2 H, J = 7.0 Hz), 5.97 (d, 1 H, J = 1.5 Hz), 6.24 (m, 1 H), 7.23 (d, 1 H, J = 1.5 Hz), and 7.25–7.38 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.4, 19.1, 27.0, 27.3, 27.8, 65.3, 77.7, 93.7, 104.8, 109.9, 120.9, 126.9, 127.7, 128.6, 129.9, 132.3, 131.0, 140.6, and 155.6.

To a solution containing 100 mg (0.7 mmol) of **53** in 35 mL of methylene chloride was added 5 mg of rhodium(II) octanoate. The reaction mixture was stirred at rt for 20 min, and then the solvent was removed under reduced pressure. The residue was chromatographed on silica gel to give 84 mg (90%) of (*Z*)-2-methyl-3-(5-(2-furyl)penten-1-yl)inden-1-one (**54**): IR (neat) 1712, 1600, 1455, and 1310 cm^{-1}; NMR (CDCl$_3$, 300 MHz) δ 1.77 (m, 2 H), 2.07 (q, 2 H, J = 7.2 Hz), 2.65 (t, 2 H, J = 7.2 Hz), 5.89 (d, 1 H, J = 1.5 Hz), 5.95 (m, 1 H), 6.12 (m, 1 H), 6.25 (m, 1 H), 6.95 (d, 1 H, J = 7.2 Hz), 7.24 (d, 1 H, J = 1.5 Hz), 7.14–7.30 (m, 2 H), and 7.38 (d, 1 H, J = 7.2 Hz); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 8.3, 27.2, 27.3, 33.5, 105.0, 109.9, 119.9, 121.9, 122.6, 127.7, 130.2, 131.7, 132.7, 140.1, 140.8, 144.6, 152.1, 155.4, and 198.8; HRMS calcd for $C_{19}H_{18}O_2$ 278.1308, found 278.1309.

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Registry No. **4**, 142458-55-7; **6**, 142458-56-8; **7**, 124583-37-5; **8a**, 124583-38-6; **8b**, 124583-39-7; **9**, 142458-57-9; **10**, 142458-58-0; **11**, 142458-59-1; **12**, 142458-60-4; (*E*)-**13**, 142458-61-5; (*Z*)-**13**, 142458-62-6; (*E*)-**14**, 142458-63-7; (*Z*)-**14**, 142458-64-8; **15**, 124583-34-2; *cis*-**16**, 142458-65-9; *trans*-**16**, 142458-66-0; **17**, 142458-67-1; **24**, 142458-68-2; **27**, 142458-69-3; **28**, 142458-70-6; **29**, 84-85-5; **30**, 41426-37-3; **31**, 36159-76-9; **32**, 142458-71-7; **35**, 142458-72-8; **36**, 142458-73-9; **44**, 138308-51-7; **45**, 142458-74-0; **46**, 142458-75-1; **51**, 142458-76-2; **52**, 142458-77-3; **53**, 142458-78-4; **54**, 142458-79-5; methyl 2-iodobenzoate, 610-97-9; 3-methyl-1-butyne, 598-23-2; methyl 2-(3-methyl-1-butynyl)benzoate, 142458-80-8; rhodium(II) mandelate, 80911-97-3; methyl 2-bromobenzoate, 610-94-6; 2-methylbutyn-2-ol, 115-19-5; methyl 2-(2-hydroxy-2-methyl-3-butyn-4-yl)benzoate, 33577-96-7; methyl 2-(2-methoxy-2-methyl-3-butyn-4-yl)benzoate, 142458-81-9; 1-ethynylcyclopentanol, 17356-19-3; methyl 2-[2-(1-hydroxycyclopentyl)ethynyl]benzoate, 142458-82-0; rhodium(II) octanoate, 68803-87-2; 1-ethynylcyclohexanol, 78-27-3; methyl 2-[2-(1-hydroxycyclohexyl)ethynyl]benzoate, 142458-83-1; 1-heptyne, 628-71-7; methyl 2-(1-heptynyl)benzoate, 118476-16-7; 4-pentyn-1-ol, 5390-04-5; allyl bromide, 106-95-6; 5-(allyloxy)-1-pentyne, 130018-34-7; methyl *o*-[5-(allyloxy)-1-pentynyl]benzoate, 142458-84-2; methyl 2-ethynylbenzoate, 33577-99-0; 2-bromo-*m*-xylene, 576-22-7; 2-bromoisophthalic acid, 22433-91-6; methyl 2-bromoisophthalate, 39622-80-5; methyl 2-ethynylisophthalate, 142458-85-3; rhodium(II) acetate, 5503-41-3; 1-bromo-3-chloropropane, 109-70-6; 1-chloro-3-furylpropane, 40517-25-7; 5-(2-furyl)-1-pentyne, 142458-86-4; methyl 2-iodophthalate, 610-97-9; methyl *o*-[5-(2-furyl)-1-pentynyl]benzoate, 142458-87-5; 6-(2-furyl)-1-hexyne, 122132-28-9; methyl-*o*-[6-(2-furyl)-1-hexynyl]benzoate, 142458-88-6; furan, 110-00-9.

Supplementary Material Available: ^{1}H-NMR and ^{13}C-NMR spectra (75 MHz) for all compounds with high-resolution mass spectra (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Comparison of the Mechanisms of the Bromination and Oxymercuration Reactions of Alkenes

Harsha B. Vardhan and Robert D. Bach*

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

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An NMR method is used to measure the formation constants for complexation of mercuric chloride and silver triflate with a series of alkenes. The trends for mercury complexation parallel the argentation constants. These data are used in a discussion of the mechanism of both the bromination and oxymercuration of alkenes. Arguments are presented that the two electrophilic addition reactions have different rate-limiting steps. In the bromination reaction the rate-determining step is the formation of a bromonium ion intermediate while oxymercuration proceeds by rate-limiting attack by solvent on a mercuronium ion intermediate in agreement with the accepted mechanism.

Introduction

The mechanistic studies to date on the mechanism of electrophilic addition to alkenes,[1] such as the bromination[2] and oxymercuration reactions,[3] have provided considerable data concerning the reactive intermediates involved, the nature of the transition state, and the stereochemistry of the addition step. The rate of bromination is strongly accelerated by alkyl substituents and retarded by electron-withdrawing substituents. Reaction with bromine normally proceeds by an antarafacial addition to nonconjugated alkenes. These observations can be satisfactorily explained on the basis of the formation of a "bromonium ion" as first postulated by Roberts and Kimball.[4a] Olah and Hockswender[4b] proposed that in a nonpolar medium a molecular complex forms which then collapses to the cyclic bromonium ion with loss of Br$^-$. The bromonium ion was observed[5a] by NMR spectroscopy at low temper-

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(1) (a) Freeman, F. *Chem. Rev.* **1975**, *75*, 439. (b) Traylor, T. G. *Acc. Chem. Res.* **1969**, *2*, 152. (c) de la Mare, P. D. B.; Bolton, R. *Electrophilic Additions to Unsaturated Systems*; Elsevier: New York, 1966. (d) Schmid, G. H.; Garrett, D. G. In *Chemistry of Alkenes*; Zabicky, J., Ed.; Wiley-Interscience: New York, 1977. (e) Fahey, R. C. In *Topics in Stereochemistry*; Eliel, E. L., Allinger, N. L., Eds.; Wiley-Interscience: New York, 1968; Vol. 3. (f) Bolton, R. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: New York, 1973; Vol. 9.

(2) (a) Dubois, J.-E.; Mouvier, G. *Bull. Soc. Chim. Fr.* **1968**, 1426. (b) de la Mare, P. B. D. *Electrophilic Halogenation*; Cambridge University Press: London, 1976. (c) Bienvenue-Goetz, E.; Dubois, J.-E. *Tetrahedron* **1978**, *3448*, 7; *J. Org. Chem.* **1975**, *40*, 221; *J. Am. Chem. Soc.* **1981**, *103*, 5388. (d) Schmid, G. H.; Tidwell, T. T. *J. Org. Chem.* **1978**, *43*, 460. (e) Modro, A.; Schmid, G. H.; Yates, K. *J. Org. Chem.* **1977**, *42*, 3673.

(3) (a) Chatt, *J. Chem. Rev.* **1951**, *48*, 7. (b) Kitching, W. *Organomet. Chem. Rev.* **1968**, *3*, 61. (c) Matteson, D. S. *Organometallic Reaction Mechanisms of the Non-transition Elements*; Academic Press: New York, 1974. (d) Kitching, W. In *Organometallic Reactions*; Becker, E. I.; Tsutsi, M., Eds.; Wiley Interscience: New York, 1972.

(4) (a) Roberts, I.; Kimball, G. E. *J. Am. Chem. Soc.* **1937**, *59*, 947. (b) Olah, G. A.; Hockswender, T. R., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 3574.

(5) (a) Olah, G. A.; Bollinger, J. M.; Brinich, J. *J. Am. Chem. Soc.* **1968**, *90*, 2587. (b) Strating, J.; Wieringo, J. H.; Wynberg, H. *J. Chem. Soc. D* **1969**, 907. (c) Slebocka-Tilk, H.; Ball, R. G.; Brown, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4504. (d) Brown, H. C.; Geoghegan, P. J., Jr. *J. Org. Chem.* **1972**, *37*, 1937. (e) Brown, H. C.; Kawakami, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 8665.