Hz) and δ 2.39 to simplify; irradiation of δ 3.22 causes δ 3.80 to collapse to a doublet, $J_{8,7}$ = 10.5 Hz, and δ 2.95 to simplify; irradiation of δ 2.95 causes δ 3.22 to collapse to a doublet, $J_{9,8}$ = 9.0 Hz; irradiation of δ 2.39 causes δ 2.72 to collapse to a doublet, $J_{12,13}$ = 12.0 Hz, and δ 3.80 to collapse to a doublet, $J_{8,9}$ = 9.0 Hz; IR (CH_2Cl_2) 3090, 3070, 3030, 2995, 2950, 2900, 2860, 1741, 1712, 1610, 1590, 1472, 1455, 1435, 1428, 1390, 1360, 1320, 1210, 1190, 1155, 1110, 1025, 920, 895 cm^{-1}; mass spectrum, *m/e* 627 ($M^+ - C_4H_9$); high-resolution mass spectrum for $C_{37}H_{43}O_7Si$ calcd 627.2777, found 627.2777.

Partial data for **69**: R_f 0.30 (40% ether–hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.64 (m, 4 H, aromatic), 7.65 (m, 11 H, aromatic), 5.73 (br d, $J_{6,5}$ = 11.0 Hz, 1 H, H_6), 5.66 (d with fine coupling, $J_{5,6}$ = 11.0 Hz, 1 H, H_5), 4.72 (AB, J_{AB} = 12.0 Hz, 1 H, H_A), 4.51 (s, 2 H), 4.50 (AB, J_{BA} = 12.0 Hz, 1 H, H_B), 3.90 (dd, *J* = 2.0, 2.0 Hz, 1 H, H_8), 3.71 (s, 3 H, methoxyl), 3.63 (m, 3 H, H_1 and probably H_9), 3.28 (m, 1 H, H_{10}), 3.25 (s, 3 H, methoxyl), 3.02 (dd, $J_{12,7}$ = $J_{12,13}$ = 10.0 Hz, 1 H, H_{12}), 2.60 (dd, $J_{13,12}$ = 10.0 Hz, $J_{13,4}$ = 6.0 Hz, H_{13}), 2.60 (m, 1 H), 2.28 (m, 1 H)8, 1.75–1.30 (m, 4 H, $H_{2,3}$), 1.10 (d, *J* = 7.0 Hz, 3 H, methyl), 1.02 (s, 9 H, *tert*-butyl).

Data for **70**: R_f 0.26 (40% ether–hexane); $[\alpha]^{23}_D$ +42.1° (*c* = 0.11, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) δ 7.64 (m, 4 H, aromatic), 7.70 (m, 11 H, aromatic), 5.92 (d, *J* = 11.0 Hz, 1 H, H_5), 5.83 (m, 1 H, H_6), 4.99 (AB, *J* = 6.5 Hz, 1 H, H_A), 4.79 (A'B', *J* = 11.0 Hz, 1 H, $H_{A'}$), 4.76 (AB, *J* = 6.5 Hz, 1 H, H_B), 4.63 (A'B', *J* = 11.0 Hz, 1 H, $H_{B'}$), 3.66 (s, 3 H, methoxyl), 3.67–3.57 (m, 3 H, H_1, H_8), 3.46 (s, 3 H, methoxyl), 3.24 (dd, $J_{9,8}$ = 9.0 Hz, $J_{9,10}$ = 10.5 Hz, 1 H, H_9), 2.87 (dd, $J_{13,12}$ = 12.0 Hz, $J_{13,4}$ = 6.5 Hz, 1 H, H_{13}), 2.80 (m, 1 H, H_{10}), 2.71 (t, *J* = 12.0 Hz, 1 H, H_{12}), 2.53 (m, 1 H, H_4), 1.98 (br t, *J* = 12 Hz, 1 H, H_7), 1.70–1.20 (m, 4 H, $H_{2,3}$), 1.15 (d, *J* = 6.5 Hz, 3 H, methyl), 1.03 (s, 9 H, *tert*-butyl); IR (CH_2Cl_2) 3070, 3060, 3050, 3030, 2995, 2950, 2930, 2890, 2860, 1736, 1722, 1610, 1590, 1472, 1438, 1428, 1390, 1360, 1350, 1325, 1200, 1178, 1110, 1025, 935, 920 cm^{-1}; mass spectrum, *m/e* 627 ($M^+ - C_4H_9$); high-resolution mass spectrum for $C_{37}H_{43}O_7Si$ calcd 627.2777, found 627.2777.

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Supplementary Material Available: A table of torsional angles for MMX-generated transition states ii, iii, v, vi, viii, ix, xi, and xii and experimental procedures for synthesis of β-keto phosphonates **31**, **42**, **61**, and **62** and phosphonium salts **16** and **40** (15 pages). Ordering information is given on any current masthead page.

Scope and Stereochemistry of the Tandem Intramolecular Cyclopropanation/Cope Rearrangement Sequence

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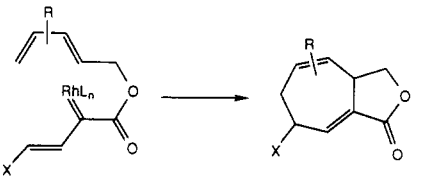
A stereoselective synthesis of a series of fused seven-membered carbocycles was achieved by a formal intramolecular 3 + 4 cycloaddition between vinylcarbenoids, generated by rhodium(II) acetate catalyzed decomposition of vinyldiazomethanes, and dienes. The products are formed by a tandem cyclopropanation/Cope rearrangement sequence rather than a concerted process.

Introduction

Highly functionalized cycloheptanes are present in a variety of important natural products, and consequently, new procedures for their formation have been actively sought.[1] As part of a general program aimed at developing new synthetic methodology based on carbenoid intermediates, we have been investigating the scope of formal 3 + 4 cycloadditions between vinylcarbenoids and dienes.[2] We have previously reported that [3.2.1] bicyclic systems are readily formed on reaction of rhodium(II)-stabilized vinylcarbenoids with furans[2a,b] or cyclopentadiene.[2c] In this paper we describe how the reaction can be extended to intramolecular systems,[2d] leading to fused cycloheptadienes of predictable stereochemistry, as shown in Scheme I.

Scheme I



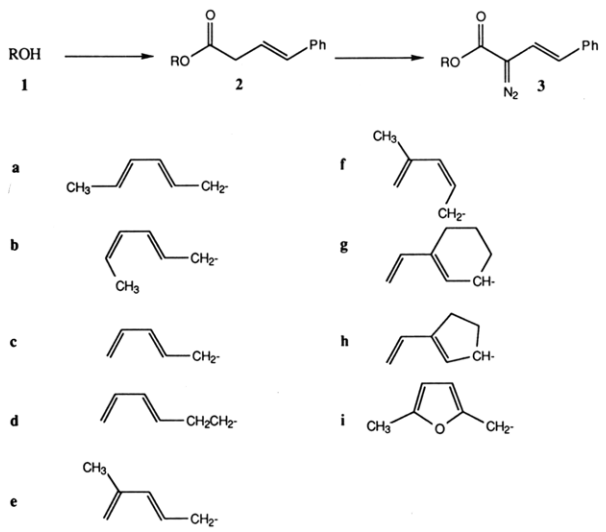
Our initial studies into the formal 3 + 4 cycloaddition between vinylcarbenoids and dienes revealed that a concerted mechanism is not involved.[2c] Instead, the reaction proceeds through a two-step sequence with initial cyclo-

(1) For examples of other 3 + 4 cycloaddition sequences for the synthesis of seven-membered rings, see: (a) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 1. (b) Noyori, R. *Acc. Chem. Res.* **1979**, *12*, 61. (c) Trost, B. M.; MacPherson, D. T. *J. Am. Chem. Soc.* **1987**, *109*, 3483.

(2) (a) Davies, H. M. L.; Clark, D. M.; Smith, T. K. *Tetrahedron Lett.* **1985**, *26*, 5659. (b) Davies, H. M. L.; Clark, D. M.; Alligood, D. B.; Eiband, G. R. *Tetrahedron* **1987**, *43*, 4265. (c) Davies, H. M. L.; Smith, H. D.; Korkor, O. *Tetrahedron Lett.* **1987**, *28*, 1853. (d) Davies, H. M. L.; Oldenburg, C. E. M.; McAfee, M. J.; Nordahl, J. G.; Henretta, J. P.; Romines, K. R. *Tetrahedron Lett.* **1988**, *29*, 975. (e) A related tandem cyclopropanation/Cope rearrangement sequence using a Fischer-carbene complex has been reported recently: Wulff, W. D.; Yang, D. C.; Murray, C. K. *J. Am. Chem. Soc.* **1988**, *110*, 2653.

0022-3263/89/1954-0930$01.50/0

Scheme II



propanation, followed by a Cope rearrangement of the resulting divinylcyclopropane. Thus, due to the stereochemical constraints of the Cope rearrangement of divinylcyclopropanes,[3] the products are formed in a stereospecific manner. Another intriguing feature of these reactions is that the cyclopropanation is highly stereoselective, forming only the *cis*-divinylcyclopropane isomer.[4] The stabilization of the carbenoid by the rhodium(II) acetate is crucial for the success of this chemistry.[2a] Earlier studies by Franck-Neumann[5] with free vinylcarbenes reacting with dienes were complicated by the tendency of vinylcarbenes to rearrange to cyclopropenes. Recently, a more stabilized vinylcarbene generated by thermolysis of a cyclopropene was developed by Boger,[6] which contained electron-donating groups. This leads to a nucleophilic vinylcarbene, which undergoes efficient reactions with electron-deficient dienes, apparently by a concerted process. Unless the diene was sterically constrained, however, the cyclopropene precursor of the vinylcarbene undergoes competing reactions.

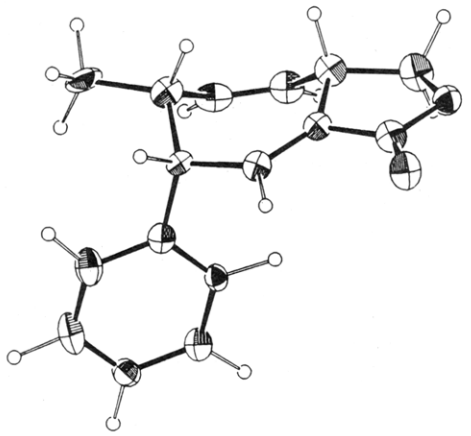


Figure 1. X-ray representation of **4a**.

Scheme III

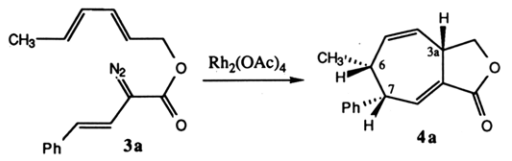


Table I. Rhodium(II) Acetate Catalyzed Decomposition of 3

entry	substrate	product	isolated yield, %
1	**3a**	**4a**	76
2	**3b**	**4b**	53
3	**3c**	**4c**	68
4	**3d**	**4d**	<5
5	**3e**	**4e**	60
6	**3f**	**5**	94
7	**3g**	**6a**	61
8	**3h**	**6b**	67
9	**3i**	**7**	71

Intramolecular cyclopropanation of dienes by simple carbenoids followed by rearrangement of the vinylcyclopropanes has been effectively used in synthesis.[7] Thermal rearrangement of vinylcyclopropanes to cyclopentenes has been extensively applied to the synthesis of triquinanes[7b] and other compounds. Alternatively, simple cleavage of the cyclopropane results in a useful annulation strategy and has been applied to the synthesis of (±)-cafestol,[7c] (±)-kahweol,[7d] and (±)-atractyligenin.[7e] Furthermore, the vinylcyclopropanes can be converted to divinylcyclopropanes, which undergo a Cope rearrangement leading to the formation of fused seven-membered rings.[3i,j]

If the extension of such reactions to vinylcarbenoids is successful, a direct and stereoselective approach to a wide range of fused seven-membered ring natural products would be available. We chose to evaluate the potential of this reaction by synthesizing a series of suitable carbenoid precursors, so that the effects of substituents, size of tether, and stereochemistry could be determined and rationalized.

Results

The first objective was to develop a general and effective synthesis of a series of suitable vinylcarbenoid precursors. An ester tether was used to join the vinyldiazomethane to

(3) For examples of the use of the Cope rearrangement of divinylcyclopropanes in organic synthesis, see: (a) Rhoads, S. J.; Raulinus, N. R. *Org. React.* **1975**, *21*, 1. (b) Marino, J. P.; Kaneko, T. *Tetrahedron Lett.* **1973**, 3975. (c) Marino, J. P.; Kaneko, T. *J. Org. Chem.* **1974**, *39*, 3175. (d) Marino, J. P.; Browne, L. J. *Tetrahedron Lett.* **1976**, 3245. (e) Piers, E.; Nagakura, I. *Tetrahedron Lett.* **1976**, 3237. (f) Piers, E.; Nagakura, I.; Morton, H. E. *J. Org. Chem.* **1978**, *43*, 3630. (g) Piers, E.; Ruediger, E. H. *J. Chem. Soc., Chem. Commun.* **1979**, 166. (h) Piers, E.; Ruediger, E. H. *J. Org. Chem.* **1980**, *45*, 1727. (i) Piers, E.; Jung, G. L.; Moss, N. *Tetrahedron Lett.* **1984**, *25*, 3959. (j) Piers, E.; Moss, N. *Tetrahedron Lett.* **1985**, *26*, 2735. (k) Wender, P. A.; Filosa, M. P. *J. Org. Chem.* **1976**, *41*, 3490. (l) Wender, P. A.; Eissenstat, M. A.; Filosa, M. P. *J. Am. Chem. Soc.* **1979**, *101*, 2196. (m) Wender, P. A.; Hillemann, C. L.; Szymonifka, M. J. *Tetrahedron Lett.* **1980**, *21*, 2205. (n) Schneider, M. P.; Rau, A. *J. Am. Chem. Soc.* **1979**, *101*, 4426 and references cited therein. (o) Cainns, P. M.; Crombie, L.; Pattenden, G. *Tetrahedron Lett.* **1982**, *23*, 1405. (p) Schotten, T.; Boland, W.; Jaenicke, L. *Tetrahedron Lett.* **1986**, *27*, 2349. (q) Sugihara, Y.; Wakabayashi, S.; Saito, N.; Murata, I. *J. Am. Chem. Soc.* **1986**, *108*, 2773. (r) Sugihara, Y.; Wakabayashi, S.; Murata, I.; Jinguiji, M.; Nakazawa, T.; Persy, G.; Winz, J. *J. Am. Chem. Soc.* **1985**, *107*, 5894. (s) Wenkert, E.; Greenberg, R. S.; Kim, H. S. *Helv. Chim. Acta* **1987**, *70*, 2159.

(4) Preference for the formation of *cis*-divinylcyclopropanes in the reaction of vinylcarbenes with dienes has been reported previously, see: Baird, M. S.; Nethercott, W. *Tetrahedron Lett.* **1983**, *24*, 605 and references cited therein.

(5) (a) Franck-Neumann, M.; Miesch, M. *Tetrahedron Lett.* **1984**, *25*, 2909. (b) Franck-Neumann, M.; Dietrich-Buchecker, C. *Tetrahedron* **1978**, *34*, 2797. (c) Franck-Neumann, M.; Lohmann, J. J. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 323.

(6) (a) Boger, D. L.; Brotherton, C. E. *J. Am. Chem. Soc.* **1986**, *108*, 6695. (b) Boger, D. L.; Brotherton, C. E. *J. Am. Chem. Soc.* **1986**, *108*, 6713. (c) Boger, D. L.; Brotherton, C. E. *J. Org. Chem.* **1985**, *50*, 3425.

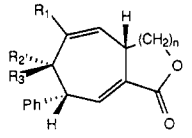
(7) (a) Burke, S. P.; Grieco, P. A. *Org. React.* **1979**, *26*, 361 and references cited therein. (b) Hudlicky, T.; Natchuz, M. G.; Zingde, G. S. *J. Org. Chem.* **1987**, *52*, 4644 and references cited therein. (c) Corey, E. J.; Wess, G.; Xiang, Y. B.; Singh, A. K. *J. Am. Chem. Soc.* **1987**, *109*, 4717. (d) Corey, E. J.; Xiang, Y. B. *Tetrahedron Lett.* **1987**, *28*, 5403. (e) Singh, A. K.; Bakshi, R. K.; Corey, E. J. *J. Am. Chem. Soc.* **1987**, *109*, 6187.

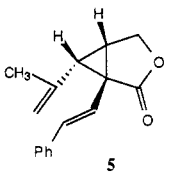
the diene system, as shown in Scheme II, in order to simplify matters. A number of dienols of specific stereochemistry were prepared by standard procedures, or slight modifications thereof, and these were esterified with 4-phenylbutenoyl chloride. Treatment of the esters **2** with *p*-acetamidobenzenesulfonyl azide,[8] a remarkably effective diazo transfer agent, resulted in clean diazotization α to the carbonyl to give **3**.

Some of the dienes could not be prepared stereochemically pure and, consequently, the resulting carbenoid precursor **3** was slightly contaminated. The *E* isomer **3e** was only 82% stereochemically pure, containing some of the *Z* isomer **3f**. (2*E*,4*Z*)-2,4-hexadienol (**1b**) was also difficult to obtain as one isomer, but the contaminating 2*E*,4*E* isomer was readily removed by reaction of impure **1b** or **2b** with tetracyanoethylene.

With suitable substrates in hand, we were able to examine the feasibility of the intramolecular reaction between vinylcarbenoids and dienes. Decomposition of the 2*E*,4*E* diene **3a** by rhodium(II) acetate in refluxing dichloromethane resulted in the formation of the fused cycloheptadiene **4a** in 76% yield (Scheme III). No evidence for any stereoisomer of **4a** was observed by NMR examination of the crude reaction mixture. Initial establishment of the stereochemistry was based on NOE difference spectra, which showed enhancements across the ring of H-3a by both H-6 and H-7. This suggests that all three protons are on the same side of the cycloheptadiene ring. This stereochemical assignment was subsequently confirmed by X-ray analysis (Figure 1).

The reaction was successful with a range of substrates and the results are summarized in Table I. When the 2*E*,4*Z* diene **3b** was used (entry 2), the resulting product **4b** differed from **4a** with respect to the chiral center at C-6. This stereochemical assignment was based on NOE difference spectra and also on the observation of a distinctive shielding of H-6 in **4b** by the adjacent phenyl group. Therefore, it appears that the stereochemistry of the product is controlled by the initial diene geometry. Similarly effective cyclizations were observed with other systems containing a five-membered ring tether between the vinylcarbenoid and the diene (entries 3, 5, 7, and 8). However, when a longer tether was used (entry 4), only a trace of the 6–7 fused product **4d** was isolated. Presumably, the additional methylene group provides the system with too much flexibility to allow effective capture of the carbenoid by the diene, resulting in the predominant formation of an intractible material.



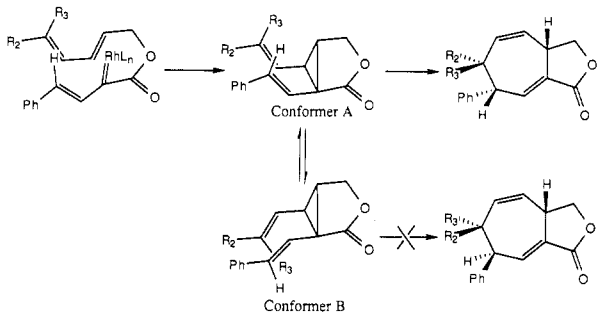


5

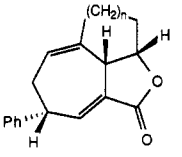
	R_1	R_2	R_3	n
4a	H	CH_3	H	1
4b	H	H	CH_3	1
4c	H	H	H	1
4d	H	H	H	2
4e	CH_3	H	H	1

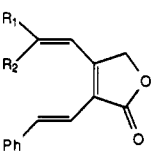
In all the cases described so far, the double bond nearest the tether has an *E* geometry. When the geometry at this double bond was *Z*, as in the case of **3f** (entry 6), a cycloheptadiene product was not formed. instead, the *trans*-divinylcyclopropane **5** was exclusively formed (94% yield). This is the first example in which we have seen any evidence for the formation of a *trans*-divinylcyclopropane intermediate in the reactions of vinylcarbenoids with dienes and the reasons for this will be discussed later. As might be expected, heating of **5** under more extreme conditions (140 °C) resulted in the clean formation of **4e**, the product obtained directly from the *E* isomer **3e** (entry 5). This is in agreement with results in the literature,[3] because it well-known that under vigorous conditions *trans*-divinylcyclopropanes are in equilibrium with the cis isomers, which would then undergo ring expansion through a Cope rearrangement.

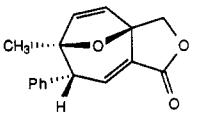
Scheme IV



The reaction can be extended to the more complex systems, **3g** and **3h**, as can be seen in entries 7 and 8.[2d] By having part of the diene contained within a ring, as is the case of **3g** and **3h**, a rapid entry into tricyclic products is obtained. The stereogenic centers in **3g** and **3h** control the direction of cyclopropanation, which translates into a specific stereochemistry for the tricyclic products **6a** and **6b**. When furan is used instead of a simple diene (**3i**, entry 9), the carbenoid is cleanly captured but trienes **7** are formed (76% yield) instead of the expected formal cycloadduct **8**. The *Z* isomer **7a** equilibrates to **7b** under the reaction conditions and this can be accelerated by the addition of iodine.[9]







	n
6a	2
6b	1

	R_1	R_2
7a	H	CH_3CO
7b	CH_3CO	H

8

Discussion

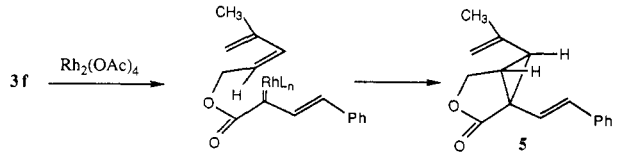
The stereospecific formation of fused cycloheptadienes can readily be rationalized by assuming that the reaction proceeds through a divinylcyclopropane intermediate. When the double bond nearest the tether is *E*, intramolecular cyclopropanation can only result in a *cis*-divinylcyclopropane, which would be expected to undergo a Cope rearrangement under very mild conditions (Scheme IV).[10] This intermediate could conceivably rearrange through two boat conformers A and B, and each would lead to a dif-

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

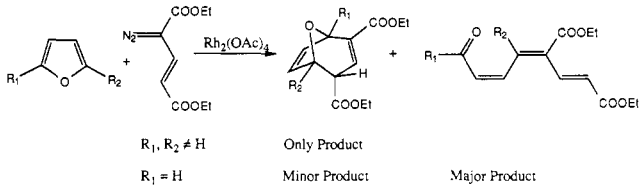
(9) Wenkert, E.; Guo, M.; Pizzo, F.; Ramachandran, K. *Helv. Chim. Acta* **1987**, *70*, 1429.

(10) Similar stereochemical results have been observed in related intramolecular cyclopropanation of simple carbenoids with (*E*,*E*)-dienes: see ref 7a,b and 3i,j.

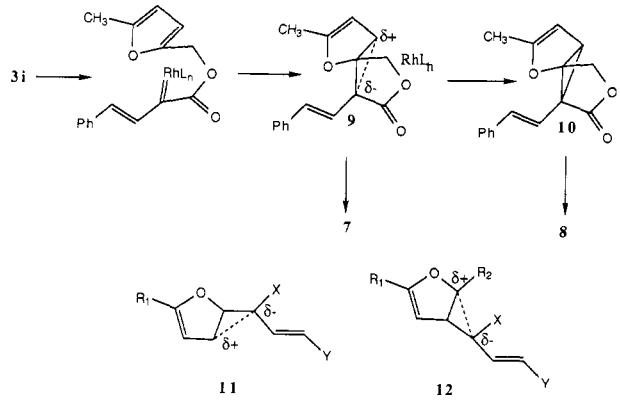
Scheme V



Scheme VI



Scheme VII



ferent product. However, it has been proposed that conformer A, in which the vinyl groups are folded back over the cyclopropane, results in greater orbital overlap,[3a,f] and rearrangement through this conformer would indeed result in the observed stereochemistry. The effectiveness of this chemistry depends on the efficiency of the cyclopropanation, and if the tether is too long (**3d**, entry 4), the fused products will not be formed.

When the double bond nearest the tether is *Z*, very clean capture of the vinylcarbenoid occurs, but as can be seen in Scheme V the expected divinylcyclopropane would be the trans isomer.[11] Even though *trans*-divinylcyclopropanes can undergo a Cope rearrangement, forcing conditions are required, and the reaciton presumably proceeds by initial rearrangement to the cis isomer.[3] Clearly, the standard conditions for the rhodium(II) acetate catalyzed decomposition of vinyldiazomethanes is not sufficiently vigorous to cause trans–cis isomerizations of divinylcyclopropanes. This would suggest that all the intermolecular systems that we have previously examined, which result in the effective formation of the formal 3 + 4 cycloadducts involve preferential generation of *cis*-divinylcyclopropane intermediates.

The formation of the trienes **7**, rather than the formal 3 + 4 cycloadduct **8**, is rather interesting because it may explain the remarkable product distribution which we have previously observed in the intermolecular reactions of vinylcarbenoids with furans.[2a,b] For example, with 2,5-disubstituted furans formal 3 + 4 cycloadducts are cleanly formed, but with 2-substituted furans trienes are the predominant products (Scheme VI). Therefore, in the intramolecular reaction with **3i**, which is a 2,5-disubstituted furan, a formal 3 + 4 cycloadduct might have been the expected product, but this was not the case. This can be explained by assuming that cyclopropanation of a furan proceeds through a somewhat dipolar transition state (**9**), as shown in Scheme VII.[12] The most reasonable structure for **9** would be the transition state of a nonsynchronous cyclopropanation as described by Doyle,[12b] but a fully dipolar structure or a metallocyclobutane[12a] are other possibilities. In the case of **3i** the cyclopropane **10** is rather strained, and consequently, the dipolar transition state preferentially undergoes rearrangement to the triene **7** rather than formation of **8** via **10**. Intermolecular reactions with 2-substituted furans would proceed through the similar transition state **11**, and thus, trienes are formed although some of the formal 3 + 4 cycloadducts are also formed in this case. Intermolecular reactions with 2,5-disubstituted furans would be expected to proceed through a different dipolar transition state (**12**) where bond formation is greatest at the β position. Rearrangement to a triene is not possible from **12** and therefore the divinylcyclopropane intermediate is formed, which undergoes a clean Cope rearrangement to the formal 3 + 4 cycloadduct. An alternative mechanism[13] in which both the triene and the formal 3 + 4 cycloadduct are derived from a common furanocyclopropane intermediate does not explain the dramatic effect of substitution pattern on product distribution.

These model studies suggest that the intramolecular reactions between vinylcarbenoids and dienes hold considerable promise for the rapid construction of fused seven-membered rings with excellent control of stereochemistry. The Cope rearrangement of divinylcyclopropanes has been extensively used in stereoselective synthesis of natural products,[3] but the construction of the divinylcyclopropane was often difficult and tedious. Clearly, the methodology described herein alleviates such problems.

The success of these intramolecular studies is in spite of the fact that these substrates are probably not the best ones to use and were chosen because of their ease of preparation. A tether without an ester linkage would be advantageous because the preferred conformation for the ester functionality is s-trans[14] while the s-cis conformer is required for the intramolecular carbenoid capture. Also vinyldiazomethanes with two strongly electron-withdrawing groups undergo cleaner reactions than 4-phenyl-2-diazobutenoates.[2d] Therefore, it is quite possible that a longer tether may be used if the functionality present is more favorable. We are in the process of further extending this chemistry by applying these stereochemical results to natural products synthesis.

Experimental Section

The X-ray analysis was carried out by Dr. John C. Huffmann at the Molecular Structure Center, Department of Chemistry, University of Indiana. The purity of all title compounds was shown to be >95% by ^{1}HNMR analysis at 200 MHz. (2*E*,4*E*)-2,4-Hexadien-1-ol (**1a**) was purchased from Aldrich Chemical Company. (2*E*,4*Z*)-2,4-Hexadien-1-ol (**1b**) was prepared

(11) Similar stereochemical results have been observed in related intramolecular cyclopropanation of simple carbenoids with (*Z*,*Z*)-dienes: see ref 7c–e.

(12) For reviews on the mechanism of reactions between metal-stabilized carbenoids and π-systems, see: (a) Maas, G. *Top. Curr. Chem.* **1987**, *137*, 75. (b) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919.

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by lithium aluminum hydride reduction of enriched (2*E*,4*Z*)-2,4-hexadien-1-al,[15] followed by treatment with tetracyanoethylene in THF for 1 h at 25 °C, to remove the undesired 2*E*,4*E* isomer. (2*E*)-2,4-Pentadien-1-ol (**1c**),[16] (3*E*)-3,5-hexadien-1-ol (**1d**),[17] (2*E*)-4-methyl-2,4-pentadien-1-ol (**1e**),[18] (2*Z*)-4-methyl-2,4-pentadien-1-ol (**1f**),[18] 3-vinyl-2-cyclohexen-1-ol (**1g**),[19] and 5-methyl-2-furanylmethanol (**1i**)[20] were prepared by literature procedures.

3-Ethenyl-2-cyclopenten-1-ol (1h). Vinylmagnesium bromide (60 mL, 1.0 M in THF, 60 mmol) was added slowly to a stirred mixture of 2-(phenylseleno)-2-cyclopenten-1-one (9.50 g, 40 mmol), copper(I) iodide (3.08 g, 16.2 mmol), and methyl sulfide (17.39 g, 280 mmol) in tetrahydrofuran (THF) (300 mL) at −40 °C under argon, following the general procedure of Vandewalle et al.[21] After stirring at −40 °C for 2 h, the reaction was quenched with a mixture of aqueous ammonia and saturated ammonium chloride solution and then extracted twice with ether. The organic phase was dried ($MgSO_4$), the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica with ether/petroleum ether (20:80) as solvent to give 3-ethenyl-2-(phenylseleno)cyclopentanone (6.23 g, 60% yield) as a 4:1 mixture of isomers.

3-Chloroperoxybenzoic acid (5.62 g, 30.2 mmol) was added in portions to a stirred solution of 3-ethenyl-2-(phenylseleno)-cyclopentanone (6.75 g, 25.9 mmol) in dichloromethane (150 mL) at 0 °C. The mixture was warmed to room temperature over 30 min and the solvent was evaporated under reduced pressure. The mixture was partitioned between ether and saturated sodium carbonate solution, the organic layer was dried ($MgSO_4$), and the solvent was then evaporated under reduced pressure. The residue was chromatographed on silica with ether/petroleum ether (10:90–40:60) as solvent gradient to give 3-ethenyl-2-cyclopenten-1-one[22] as a pale yellow gum: 2.33 g (93% yield); ^{1}H NMR ($CDCl_3$) δ 6.84 (dd, 1 H, J = 17.5, 10.6 Hz), 6.10 (s, 1 H), 5.80 (d, 1 H, J = 17.5 Hz), 5.56 (d, 1 H, J = 10.6 Hz), 2.77 (m, 2 H), 2.48 (m, 2 H).

Sodium borohydride (0.40 g, 10.6 mmol) was added in small portions to a stirred mixture of 3-ethenyl-2-cyclopenten-1-one (1.14 g, 10.6 mmol) and cerium(III) chloride heptahydrate[23] (3.92 g, 10.6 mmol) in methanol (30 mL), while the temperature was maintained below 7 °C. After being stirred for a further 5 min, the mixture was quenched with aqueous ammonium chloride (75 mL) and then extracted with ether. The organic layer was dried ($MgSO_4$), the solvent was evaporated under reduced pressure, and the residue was purified by Kugelrohr distillation to give **1h**[2d,24] as a colorless liquid: 0.79 g (68% yield); IR (neat) 3340, 1630, 1590 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.58 (dd, 1 H, J = 17.4, 10.6 Hz), 5.76 (s, 1 H), 5.23 (d, 1 H, J = 17.4 Hz), 5.19 (d, 1 H, J = 10.6 Hz), 4.89 (br d, 1 H, J = 5.4 Hz), 2.62 (m, 1 H), 2.35 (m, 2 H), 1.75 (m, 1 H), 1.63 (br s, 1 H).

General Procedure for the Preparation of the Esters 2. A solution of 4-phenyl-3-butenoyl chloride (1.5 equiv) in dry dichloromethane was added to a stirred solution of the alcohol **1** (1.0 equiv), pyridine (2.0 equiv), and 4-(dimethylamino)pyridine (DMAP) (0.05 equiv) in dry dichloromethane at 0 °C. After being slowly warmed to 25 °C and stirred for 12 h, the mixture was washed with saturated ammonium chloride solution and dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica.

(2*E*,4*E*)-2,4-Hexadienyl 4-Phenyl-3-butenoate (2a). The crude product was purified by chromatography on silica with ether/petroleum ether (10:90) as solvent to give **2a** as a colorless solid: 66% yield, mp 32–34 °C; IR (Nujol) 1745 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.40–7.22 (m, 5 H), 6.49 (d, 1 H, J = 15.9 Hz), 6.29 (dt, 1 H, J = 15.9, 6.3 Hz), 6.26 (superimposed m, 1 H), 6.05 (m, 1 H), 5.80–5.59 (d, 2 H, J = 6.5 Hz), 4.61 (d, 2 H, J = 6.5 Hz), 3.25 (d, 2 H, J = 6.5 Hz), 1.76 (d, 3 H, J = 6.6 Hz); MS m/z (relative intensity) 242 (0.9), 117 (100), 104 (10), 91 (22), 81 (81), 53 (20); HRMS calcd for $C_{16}H_{18}O_2$ 242.1307, found 242.1308.

(2*E*,4*Z*)-2,4-Hexadienyl 4-Phenyl-3-butenoate (2b). The crude product was purified by column chromatography on silica with ether/petroleum ether (2:98–5:95) as solvent to give **2b** as a colorless gum: 57% yield; IR (neat) 1715, 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.39–7.19 (m, 5 H), 6.65 (dd, 1 H, J = 14.8, 11.6 Hz), 6.50 (d, 1 H, J = 16.0 Hz), 6.30 (dt, 1 H, J = 16.0, 6.9 Hz), 6.02 (dd, 1 H, J = 11.6, 10.1 Hz), 5.80–5.56 (m, 2 H), 4.67 (d, 2 H, J = 6.6 Hz), 3.27 (d, 2 H, J = 6.8 Hz), 1.75 (d, 3 H, J = 7.1 Hz); MS m/z (relative intensity) 242 (4), 162 (5), 146 (20), 117 (97), 81 (100), 53 (14); HRMS calcd for $C_{16}H_{18}O_2$ 242.1307, found 242.1302.

(2*E*)-2,4-Pentadienyl 4-Phenyl-3-butenoate (2c). (2*E*)-2,4-Pentadienol (**1c**) was used without further purification and the crude product was purified by column chromatography on silica with ether/petroleum ether (5:95–30:70) as solvent gradient to give **2c** as a colorless gum: 20% overall yield from pentadienoic acid: R_f = 0.08 (ether/petroleum ether (10:90)); IR (neat) 1720, 1595, 1485 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.39–7.20 (m, 5 H), 6.51 (d, 1 H, J = 15.9 Hz), 6.39–6.13 (m, 3 H), 5.80 (dt, 1 H, J = 14.6, 6.2 Hz), 5.22 (d, 1 H, J = 15.6 Hz), 5.17 (d, 1 H, J = 8.6 Hz), 4.66 (d, 2 H, J = 6.2 Hz), 3.28 (d, 2 H, J = 6.6 Hz); MS m/z (relative intensity) 228 (3), 162 (2), 146 (12), 117 (100), 104 (13), 91 (12), 77 (3), 67 (47), 51 (3); HRMS calcd for $C_{15}H_{16}O_2$ 228.1151, found 228.1144.

(3*E*)-3,5-Hexadienyl 4-Phenyl-3-butenoate (2d). The crude product was purified by column chromatography on silica with ether/petroleum ether (10:90) as solvent to give **2d** as a gum: 94% yield: R_f 0.6 (ether/petroleum ether (10:90)); IR (neat) 1710, 1590 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.40–7.22 (m, 5 H), 6.50 (d, 1 H, J = 15.9 Hz), 6.41–6.06 (m, 3 H), 5.66 (dt, 1 H, J = 15.2, 6.9 Hz), 5.12 (d, 1 H, J = 16.0 Hz), 5.02 (d, 1 H, J = 8.3 Hz), 4.17 (t, 2 H, J = 6.9 Hz), 3.25 (d, 2 H, J = 6.8 Hz), 2.44 (dt, 2 H, J = 7.0, 6.8 Hz); MS m/z (relative intensity) 242 (0.5), 162 (0.3), 151 (4), 117 (92), 91 (14), 80 (100); HRMS calcd for $C_{16}H_{18}O_2$ 242.1307, found 242.1310.

(2*E*)-4-Methyl-2,4-pentadienyl 4-Phenyl-3-butenoate (2e). The crude product was purified by column chromatography on silica with ether/petroleum ether (5:95–10:90) as solvent gradient to give **2e** (contaminated with about 20% of the *Z* isomer) as a gum: 73% yield; R_f 0.6 (ether/petroleum ether (10:90)); IR (neat) 1730, 1650, 1608 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.40–7.19 (m, 5 H), 6.51 (d, 1 H, J = 15.9 Hz), 6.39 (d, 1 H, J = 16.1 Hz), 6.31 (dt, 1 H, J = 15.9, 6.2 Hz), 5.74 (dt, 1 H, J = 16.1, 6.6 Hz), 5.02 (br s, 2 H), 4.69 (d, 2 H, J = 6.6 Hz), 3.28 (d, 2 H, J = 6.2 Hz), 1.86 (s, 3 H); MS m/z (relative intensity) 144 (12), 117 (100), 104 (9), 91 (15), 81 (30), 65 (4); HRMS calcd for $C_{16}H_{18}O_2$ 242.1307, found 242.1310.

(2*Z*)-4-Methyl-2,4-pentadienyl 4-Phenyl-3-butenoate (2f). The crude product was purified by column chromatography on silica with ether/petroleum ether (5:95) as solvent to give **2f** as a gum: 87% yield; R_f 0.6 (ether/petroleum ether (10:90)); IR (neat) 1750, 1630, 1592 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.40–7.25 (m, 5 H), 6.50 (d, 1 H, J = 15.8 Hz), 6.30 (dt, 1 H, J = 15.8, 6.5 Hz), 6.06 (d, 1 H, J = 11.6 Hz), 5.56 (dt, 1 H, J = 11.6, 7.5 Hz), 5.05 (br s, 1 H), 4.85 (d, 2 H, J = 7.5 Hz), 4.83 (br s, 1 H), 3.27 (d, 2 H, J = 6.5 Hz), 1.87 (s, 3 H); MS, m/z (relative intensity) 242 (1), 146 (10), 117 (100), 104 (9), 97 (1), 91 (10), 81 (51); HRMS calcd for $C_{16}H_{18}O_2$ 242.1307, found 242.1314.

3-Ethenyl-2-cyclohexenyl 4-Phenyl-3-butenoate (2g).[2d] The crude product was purified by chromatography with ether/petroleum ether (20:80) as solvent to give **2g** as a colorless gum: 91% yield; R_f 0.8 (ether/petroleum ether (20:80)); IR (neat) 1720, 1605, 1490 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.40–7.17 (m, 5 H), 6.49 (d, 1 H, J = 15.9 Hz), 6.36 (dd, 1 H, J = 17.7, 10.7 Hz), 6.30 (dt, 1 H, J = 15.9, 6.8 Hz), 5.73 (br d, 1 H, J = 3.7 Hz), 5.41 (br d, 1 H, J = 3.7 Hz), 5.25 (d, 1 H, J = 17.7 Hz), 5.08 (d, 1 H, J = 10.7 Hz), 3.24 (d, 2 H, J = 6.8 Hz), 2.35–2.03 (m, 2 H), 1.95–1.65 (m, 4 H). Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.45; H, 7.47.

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3-Ethenyl-2-cyclopentenyl 4-Phenyl-3-butenoate (2h).[2d] Due to the instability of **2h** to chromatography, the residue was triturated with ethanol/water (1:1) to give **2h** as a pale yellow solid: 43% yield; mp 40–47 °C; R_f 0.7 (ether/petroleum ether (20:80)); IR (neat) 1720, 1598, 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.17 (m, 5 H), 6.59 (dd, 1 H, J = 18.1, 10.6 Hz), 6.48 (d, 1 H, J = 15.5 Hz), 6.29 (dt, 1 H, J = 15.5, 6.9 Hz), 5.77 (br s, 2 H), 5.25 (d, 1 H, J = 18.1 Hz), 5.23 (d, 1 H, J = 10.5 Hz), 3.22 (d, 2 H, J = 6.9 Hz), 2.72–2.55 (m, 1 H), 2.48–2.30 (m, 2 H), 2.05–1.80 (m, 1 H). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.37; H, 7.14.

(5-Methyl-2-furanyl)methyl 4-Phenyl-3-butenoate (2i). The crude product was purified by chromatography on silica with ether/petroleum ether (5:95–10:90) as solvent gradient to give **2i** as a gum: 86% yield; R_f 0.3 (ether/petroleum ether (5:95)); IR (neat) 1728, 1594, 1556, 1488 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.22 (m, 5 H), 6.49 (d, 1 H, J = 15.9 Hz), 6.30 (dt, 1 H, J = 15.9, 6.6 Hz), 6.31 (superimposed d, 1 H, J = 2.7 Hz), 5.96 (d, 1 H, J = 2.7 Hz), 5.05 (s, 2 H), 3.28 (d, 2 H, J = 6.6 Hz), 2.31 (s, 3 H). Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.91; H, 6.30.

General Procedure for Preparation of Diazomethanes 3. A solution of 1,8-diazabicyclo[5.4.0]undec-7-enone (DBU) (5 mmol) in acetonitrile (10 mL) was added to a stirred solution of the ester **2** (5 mmol) and *p*-acetamidobenzenesulfonyl azide (5 mmol) in acetonitrile (10 mL) at 0 °C. After stirring for 4 h at 0 °C, a saturated ammonium chloride solution (50 mL) was added, and the mixture was extracted with dichloromethane (25 mL). The organic layer was dried ($MgSO_4$), the solvent was evaporated under reduced pressure, and the residue was triturated with petroleum ether to remove the *p*-acetamidobenzenesulfonamide. The residue was purified by chromatography on silica. Unless the products were crystalline, they were of insufficient stability to obtain HRMS or elemental analysis.

(2*E*,4*E*)-2,4-Hexadienyl 2-Diazo-4-phenyl-3-butenoate (3a). The crude product was purified by column chromatography on alumina with ether/hexane (10:90) as solvent to give **3a** as an orange solid: 82% yield; mp 60–62 °C; IR (Nujol) 2090, 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.44–7.12 (m, 5 H), 6.48 (d, 1 H, J = 16.4 Hz), 6.18 (d, 1 H, J = 16.4 Hz), 6.37–6.00 (superimposed m, 2 H), 5.86–5.59 (m, 2 H), 4.76 (d, 2 H, J = 6.5 Hz), 1.78 (d, 3 H, J = 6.6 Hz). Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.51; H, 6.06; N, 10.37.

(2*E*,4*Z*)-2,4-Hexadienyl 2-Diazo-4-phenyl-3-butenoate (3b). The crude product was purified by column chromatography on silica with ether/petroleum ether (15:85) as solvent to give **3b** as an orange oil: 62% yield; R_f 0.7 (ether/petroleum ether (15:85)); IR (neat) 2078, 1690, 1620, 1437 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38–7.14 (m, 5 H), 6.64 (dd, 1 H, J = 15.9, 10.7 Hz), 6.49 (d, 1 H, J = 16.1 Hz), 6.19 (d, 1 H, J = 16.1 Hz), 6.03 (ddd, 1 H, J = 10.7, 10.7, 1.8 Hz), 5.83–5.56 (m, 2 H), 4.80 (d, 2 H, J = 6.6 Hz), 1.78 (d, 3 H, J = 7.1 Hz).

(2*E*)-2,4-Pentadienyl 2-Diazo-4-phenyl-3-butenoate (3c). The crude product was purified by column chromatography on silica with ether/petroleum ether (10:90) as solvent to give **3c** as an orange solid: 81% yield; mp 34–38 °C; R_f 0.85 (ether/petroleum ether (15:85)); IR (neat) 2065, 1678, 1618, 1483 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.39–7.17 (m, 5 H), 6.49 (d, 1 H, J = 16.3 Hz), 6.41–6.31 (m, 2 H), 6.20 (d, 1 H, J = 16.3 Hz), 5.81 (dt, 1 H, J = 14.6, 6.0 Hz), 5.29 (d, 1 H, J = 15.6 Hz), 5.18 (d, 1 H, J = 9.1 Hz), 4.79 (d, 2 H, J = 6.0 Hz); MS m/z (relative intensity) 254 (30), 209 (12), 191 (36), 171 (97), 144 (4), 114 (53), 89 (9), 77 (16), 67 (100), 51 (16); HRMS calcd for $C_{15}H_{14}O_2N_2$ 254.1052, found 254.1059.

(3*E*)-3,5-Hexadienyl 2-Diazo-4-phenyl-3-butenoate (3d). The crude product was purified by column chromatography on silica with ether/petroleum ether (15:85) as solvent to give **3d** as an orange gum: 87% yield; R_f 0.75 (ether/petroleum ether (15:85)); IR (neat) 2080, 1690, 1550, 1495 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38–7.19 (m, 5 H), 6.48 (d, 1 H, J = 16.3 Hz), 6.42–6.09 (superimposed m, 2 H), 6.22 (d, 1 H, J = 16.3 Hz), 5.67 (dt, 1 H, J = 14.9, 7.1 Hz), 5.16 (d, 1 H, J = 15.1 Hz), 5.04 (d, 1 H, J = 8.3 Hz), 4.30 (t, 2 H, J = 6.7 Hz), 2.48 (dt, 2 H, J = 7.1, 6.7 Hz).

(2*E*)-4-Methyl-2,4-pentadienyl 2-Diazo-4-phenyl-3-butenoate (3e). The crude product was purified by column chromatography on silica with ether/petroleum ether (15:85) as solvent to give **3e** (contaminated with 18% of the *Z* isomer **3f**) as an orange gum: 86% yield; R_f 0.7 (ether/petroleum ether (15:85)); IR (neat) 2055, 1690, 1618, 1603, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.44–7.16 (m, 5 H), 6.49 (d, 1 H, J = 16.4 Hz), 6.41 (d, 1 H, J = 16.1 Hz), 6.20 (d, 1 H, J = 16.4 Hz), 5.76 (dt, 1 H, J = 16.1, 6.5 Hz), 5.05 (br s, 2 H), 4.82 (d, 2 H, J = 6.5 Hz), 1.87 (s, 3 H).

(2*Z*)-4-Methyl-2,4-pentadienyl 2-Diazo-4-phenyl-3-butenoate (3f). The crude product was purified by column chromatography on silica with ether/petroleum ether (15:85) as solvent to give **3f** as an orange gum: 83% yield; R_f 0.7 (ether/petroleum ether (15:85); IR (Nujol) 2055, 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.44–7.18 (m, 5 H), 6.48 (d, 1 H, J = 16.0 Hz), 6.19 (d, 1 H, J = 16.0 Hz), 6.09 (d, 1 H, J = 11.1 Hz), 5.59 (dt, 1 H, J = 11.1, 6.6 Hz), 5.07 (br s, 1 H), 4.98 (d, 2 H, J = 6.6 Hz), 4.83 (br s, 1 H), 1.89 (s, 3 H).

3-Ethenyl-3-cyclohexenyl 2-Diazo-4-phenyl-3-butenoate (3g).[2d] The crude product was purified on silica with ether/petroleum ether (20:80) as solvent to give **3g** as an orange gum: 81% yield; R_f 0.7 (ether/petroleum ether (20:80)); IR (neat) 2080, 1687, 1624, 1602 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.17 (m, 5 H), 6.48 (d, J = 16.7 Hz, 1 H), 6.37 (dd, J = 17.4, 10.7 Hz, 1 H), 6.18 (d, J = 16.7 Hz, 1 H), 5.76 (br s, 1 H), 5.55 (m, 1 H), 5.27 (d, J = 17.4 Hz, 1 H), 5.10 (d, J = 10.7 Hz, 1 H), 2.35–2.03 (m, 2 H), 1.95–1.65 (m, 4 H).

3-Ethenyl-2-cyclopentenyl 2-Diazo-4-phenyl-3-butenoate (3h).[2d] The orange-colored crude product was essentially pure by NMR. **3h** decomposed on attempted purification by chromatography and was used directly in subsequent reactions: 48% yield; IR (neat) 2090, 1695, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.14 (m, 5 H), 6.60 (dd, J = 17.7, 10.5 Hz, 1 H), 6.48 (d, J = 16.4 Hz 1 H), 6.17 (d, J = 16.4 Hz, 1 H), 5.89 (br d, J = 6.2 Hz, 1 H), 5.80 (br s, 1 H), 5.29 (d, J = 17.7 Hz), 5.25 (d, J = 10.5 Hz, 1 H), 2.72–2.55 (m, 1 H), 2.48–2.30 (m, 2 H), 2.05–1.80 (m, 1 H).

(5-Methyl-2-furanyl)methyl 2-Diazo-4-phenyl-3-butenoate (3i). The crude product was purified on silica with ether/petroleum ether (15:85) as solvent to give **3i** as an orange gum: 81% yield; R_f 0.7 (ether/petroleum ether (15:85)); IR (neat) 2095, 1695, 1568, 1454 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38–7.18 (m, 5 H), 6.48 (d, 1 H, J = 16.4 Hz), 6.33 (d, 1 H, J = 3.1 Hz), 6.17 (d, 1 H, J = 16.4 Hz), 5.95 (d, 1 H, J = 3.1 Hz), 5.17 (s, 2 H), 2.31 (s, 3 H).

General Procedure for the Rhodium(II) Acetate Catalyzed Decomposition of 3. A solution of **3** (5 mmol) in dichloromethane (10 mL) was added dropwise over 10 min to a stirred mixture of rhodium(II) acetate (0.021 g, 0.05 mmol) in dry dichloromethane (10 mL) and heated under reflux in an argon atmosphere. After heating for a further 10 min, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica.

(3aα,6α,7α)-(±)-3,3a,6,7-Tetrahydro-6-methyl-7-phenyl-1*H*-cyclohepta[*c*]furan-1-one (4a). The crude product from the rhodium(II) acetate catalyzed decomposition of **3a** was purified by column chromatography on silica with ethyl acetate/hexane (10:90) as solvent to give **4a** as a white solid. The X-ray sample was prepared by recrystallization from ethyl acetate/hexane: 76% yield; mp 104–106 °C; IR (Nujol) 1755, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25–7.13 (m, 5 H), 6.92 (dd, 1 H, J = 5.3, 3.2 Hz), 5.68 (ddd, 1 H, J = 10.0, 2.1, 2.1 Hz), 5.36 (ddd, 1 H, J = 10.0, 6.4, 3.0 Hz), 4.66 (dd, 1 H, J = 8.7, 8.7 Hz) 4.21 (m, 1 H), 4.09 (dd, 1 H, J = 8.7, 8.7 Hz) 3.69 (m, 1 H), 3.16 (m, 1 H), 1.00 (d, 3 H, J = 6.7 Hz). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.99; H, 6.75.

(3aα,6β,7α)-(±)-3,3a,6,7-Tetrahydro-6-methyl-7-phenyl-1*H*-cyclohepta[*c*]furan-1-one (4b). The crude product from the rhodium(II) acetate catalyzed decomposition of **3b** was purified by column chromatography on silica with ether/petroleum ether (5:95–20:80) as solvent gradient to give **4b** as a colorless gum: 53% yield; R_f 0.2 (ether/petroleum ether (10:90)); IR (neat) 1730, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.37–7.17 (m, 5 H), 7.05 (dd, 1 H, J = 5.7, 3.3 Hz), 5.63 (ddd, 1 H, J = 11.7, 3.8, 2.9 Hz), 5.42 (ddd, 1 H, J = 11.7, 1.7, 1.7 Hz), 4.65 (dd, 1 H, J = 9.5, 7.8 Hz), 4.12 (m, 1 H), 3.98 (t, 1 H, J = 8.3 Hz), 3.66 (ddd, 1 H, J = 8.7, 6.1, 2.7 Hz), 2.62 (m, 1 H), 0.91 (d, 3 H, J = 7.1 Hz); MS m/z (relative intensity) 240 (67), 185 (61), 165 (47), 157 (33), 141 (21), 126 (70), 115 (37), 104 (56), 91 (50), 77 (35), 69 (42), 55 (100); HRMS calcd for $C_{16}H_{16}O_2$ 240.1151, found 240.1152.

(3aα,7α)-(±)-3,3a,6,7-Tetrahydro-7-phenyl-1*H*-cyclohepta[*c*]furan-1-one (4c). The crude product from the rho-

dium(II) acetate catalyzed decomposition of **3c** was purified by column chromatography on silica with ether/petroleum ether (10:90–30:70) as solvent gradient to give **4c** as a white solid: 68% yield; mp 124–127 °C; IR (Nujol) 1730, 1668 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.37–7.19 (m, 5 H), 7.04 (dd, 1 H, J = 4.5, 4.1 Hz), 5.72 (ddd, 1 H, J = 11.1, 5.6, 2.3 Hz), 5.62 (br d, 1 H, J = 11.1 Hz), 4.66 (t, 1 H, J = 8.6 Hz), 4.23 (m, 1 H), 4.05 (t, 1 H, J = 8.6 Hz), 3.98 (m, 1 H), 2.83 (br d, 1 H, J = 15.6 Hz), 2.49 (br d, 1 H, J = 15.6 Hz); MS m/z (relative intensity) 226 (9), 181 (28), 167 (84), 153 (37), 141 (26), 128 (35), 115 (54), 104 (60), 91 (100), 77 (25), 63 (10); HRMS calcd for $C_{15}H_{14}O_2$ 226.0994, found 226.0979.

(3aα,7α)-(±)-3,3a,6,7-Tetrahydro-5-methyl-7-phenyl-1*H*-cyclohepta[*c*]furan-1-one (4e). The diazo precursor **3e** was a 82:18 mixture of *E* and *Z* isomers and the crude product was purified by column chromatography on silica with ether/petroleum ether (20:80) as solvent to give a mixture of **4e** and **5** in 73% yield (75:25 ratio). The mixture could be cleanly converted to **4e** by being heated at 140 °C in xylene for 10 min: R_f 0.2 (ether/petroleum ether (20:80)); ^1H NMR ($CDCl_3$) δ 7.35–7.15 (m, 5 H), 6.93 (m, 1 H), 5.37 (br s, 1 H), 4.63 (t, 1 H, J = 8.1 Hz), 4.14 (m, 1 H), 4.03 (t, 1 H, J = 8.1 Hz), 3.91 (m, 1 H), 3.02 (br d, 1 H, J = 14.4, Hz), 2.23 (dd, 1 H, J = 14.4, 5.4 Hz), 1,26 (s, 3 H); MS m/z (relative intensity) 240 (17), 195 (13), 181 (41), 165 (33), 129 (17), 119 (29), 105 (82), 91 (100), 77 (42), 61 (31); HRMS calcd for $C_{16}H_{16}O_2$ 240.1151, found 240.1152.

1-(2-Phenylethenyl)-6-(2-propenyl)-3-oxabicyclo[3.1.0]hexan-2-one (5). The crude product from the rhodium(II) acetate catalyzed decomposition of **3f** was purified by column chromatography on silica with ether/petroleum ether (20:80) as solvent to give **5** as a gum: 94% yield; R_f 0.8 (ether/petroleum ether (20:80)); IR (Nujol) 1735, 1635, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35–7.23 (m, 5 H), 6.61 (d, 1 H, J = 16.1 Hz), 6.45 (d, 1 H, J = 16.1 Hz), 5.07 (br s, 1 H), 5.00 (br s, 1 H), 4.40 (dd, 1 H, J = 10.0, 5.2 Hz), 4.21 (d, 1 H, J = 10.0 Hz), 2.63 (dd, 1 H, J = 9.1, 5.2 Hz), 2.31 (br d, 1 H, J = 9.1 Hz), 1.85 (s, 3 H). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.00; H, 6.73.

(4α,9aα,9bα)-(±)-5,7,8,9,9a,9b-Hexahydro-4-phenyl-4*H*-cyclohepta[*cd*]benzofuran-2-one (6a).[2d] The crude product from the rhodium(II) acetate catalyzed decomposition of **3g** was purified by column chromatography with ether/petroleum ether (50:50) as solvent to give **6a** as a pale yellow gum: 61% yield; R_f 0.25 (ether/petroleum ether (20:80)); IR (neat) 1745, 1667, 1599, 1488 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.14 (m, 5 H), 6.99 (dd, 1 H, J = 4.5, 3.5 Hz), 5.35 (m, 1 H), 4.80 (ddd, 1 H, J = 8.6, 8.6, 4.6 Hz), 4.27 (m, 1 H), 3.90 (m, 1 H), 2.81 (br d, 1 H, J = 14.5 Hz), 2.36 (dd, 1 H, J = 14.5, 7.1 Hz), 2.25 (m, 2 H), 1.98 (m, 1 H), 1.73–1.48 (m, 3 H); MS m/z (relative intensity) 266 (31), 222 (100), 221 (48), 209 (18), 195 (30), 179 (41), 167 (48), 165 (53), 91 (64), 77 (36); HRMS calcd for $C_{18}H_{18}O_2$ 266.1306, found 266.1297.

(4α,8aα,8bα)-(±)-4,5,7,8,8a,8b-Hexahydro-4-phenyl-2*H*-azuleno[1,8-*bc*]furan-2-one (6b).[2d] The crude product from the rhodium(II) acetate catalyzed decomposition of **3h** was purified by column chromatography with ether/petroleum ether (10:90–40:60) as solvent gradient to give **6b** as a pale yellow gum: 67% yield; IR (neat) 1745, 1660, 1584, 1520 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.14 (m, 5 H), 6.86 (dd, 1 H, J = 7.8, 3.9 Hz), 5.41 (m, 1 H), 5.08 (ddd, 1 H, J = 9.2, 7.1, 7.1 Hz), 4.20 (m, 1 H), 3.96 (m, 1 H), 2.85 (br d, 1 H, J = 15.5 Hz), 2.49–2.26 (m, 4 H), 1.70 (m, 1 H); MS m/z (relative intensity) 252 (18), 208 (100), 193 (12), 179 (43), 165 (46), 128 (29), 117 (29), 91 (37), 77 (25); HRMS calcd for $C_{17}H_{16}O_2$ 252.1150, found 252.1129.

4-(2-Acetylethenyl)-3-(2-phenylethenyl)furan-2(5*H*)-one (7). The crude product from the rhodium(II) acetate catalyzed decomposition of **3i** was a mixture of cis and trans isomers that slowly equilibrated to the trans isomer on treatment with iodine in dichloromethane for 12 h. After treatment with decolorizing carbon, the solvent was removed under reduced pressure and the residue was triturated with ether to give **7** as a yellow solid: 71% yield; mp 162–165 °C; IR (Nujol) 1750, 1684, 1602, 1563 cm^{-1}; ^1H NMR ($CDCl_3$) δ trans isomer 8.05 (d, 1 H, J = 16.1 Hz), 7.68 (d, 1 H, J = 16.0 Hz), 7.59–7.49 (m, 2 H), 7.43–7.25 (m, 3 H), 6.90 (d, 1 H, J = 16.0 Hz), 6.35 (d, 1 H, J = 16.1 Hz), 4.95 (s, 2 H), 2.41 (s, 3 H); cis isomer 7.95 (d, 1 H, J = 16.0 Hz), 7.59–7.49 (m, 2 H), 7.43–7.25 (m, 3 H), 7.01 (d, 1 H, J = 16.0 Hz), 6.82 (d, 1 H, J = 11.6 Hz), 6.42 (d, 1 H, J = 11.6 Hz), 5.13 (s, 2 H), 2.33 (s, 3 H); MS m/z (relative intensity) 254 (59), 212 (100), 194 (23), 183 (17), 165 (29), 121 (38), 105 (25), 81 (32), 69 (71), 57 (29); HRMS calcd for $C_{16}H_{14}O_3$ 254.0943, found 254.0948.

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Supplementary Material Available: Crystallographic data including tables of the atomic positional and thermal parameters, bond distances, and bond angles for **4a** (9 pages). Ordering information is given on any current masthead page.