117.6, 157.2 (CH=CH), 135.9 (q). Anal. Calcd for $C_{27}H_{28}Si$: C, 85.21; H, 7.42. Found: C, 85.51; H, 7.18.

(*E*)-*exo*-7-[2-(Trimethylsilyl)-1-vinyl]bicyclo[4.1.0]heptane (9h) from 5k: eluent PE/ethyl acetate (7:1); oil (64%); IR (neat) 3010, 1610, 1245, 860, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.01 (s, 9 H), 1.01 (m, 2 H), 1.12-1.33 (m, 5 H), 1.68-1.89 (m, 4 H), 5.53 (dd, J = 6.9, 18.2, 1 H), 5.55 (dd, J = 1.0, 18.2, 1 H); ^{13}C NMR ($CDCl_3$) δ -0.99 ($Si(CH_3)_3$), 20.4 (CH), 21.5, 23.3 (CH_2), 30.8 (CH), 124.8, 151.0 (CH=CHSi); MS m/z (relative intensity) 194 (M^+, 9), 179 (11), 120 (31), 73 (100). Anal. Calcd for $C_{12}H_{22}Si$: C, 74.14; H, 11.41. Found: C, 74.00; H, 11.24.

(*E*/*Z*)-7-[2-(Phenylthio)ethenyl]bicyclo[4.1.0]heptane (9i) from **5i** (67%, *E*/*Z** ratio 1:1*); from **5j** (90%, *E*/*Z* ratio 8:1). Column chromatography on silica using hexane provided a pure product: IR (neat) 3050, 3000, 1605, 1585, 740, 685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90-1.2 (m, 6 H), 1.55 (dt, J = 4.4, 9.4, 1 H (*Z*), the corresponding signal for the *E* isomer is overlapping with the cyclohexyl protons), 1.60-2.0 (m, 4 H), 5.31* (t, J = 9.4, 1 H), 5.59 (dd, J = 9.2, 14.8, 1 H), 6.02*, 6.05 (d, J = 9.4*, 14.8, 1 H), 7.10-7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 20.3, 20.5* (CH), 21.3, 21.4*, 23.1, 23.2* (CH_2), 24.9*, 27.6 (CH), 115.4*, 117.6 (CH=CHSPh), 125.6, 125.7, 127.8, 128.2, 128.8, 128.9 (arom), 137.1*, 137.5 (q), 139.5, 143.3* (CH=CHSPh). Anal. Calcd for $C_{15}H_{18}S$: C, 78.21; H, 7.87; S, 13.92. Found: C, 78.25; H, 8.01; S, 13.79.

Vinylcyclopropane 9b from Epoxide 1b. See general procedure for in situ formation of tosylates (method B). Prior to work up of the reaction mixture after the tosylation step, another 1.5 equiv of *n*-BuLi was added, and the reaction was carried on as described above. Yield: 50%.

General Procedure for the Preparation of Vinylcyclopropanes 9 Using Tetrabutylammonium Fluoride (TBAF). At room temperature, 1 equiv of the tosylate in THF (10 mL/mmol) was treated with 1.1 equiv of TBAF in THF (5 mL/mmol). After 15 min, the reddish brown solution was poured into a 1:1 mixture of brine and hexane. The organic layer was washed twice with saturated brine, dried ($MgSO_4$), and concentrated in vacuo.

***endo*/*exo*-6-[2-(Trimethylsilyl)-1-vinyl]bicyclo[3.1.0]hexane (9g, Endo*/Exo Ratio 1*:3).** The crude product was distilled in a Kugelrohr apparatus ($bp_{0.05}$ 55 °C). The distillate was purified by column chromatography on silica gel using hexane to give a colorless oil (54%): IR (neat) 3030, 1605, 1240, 860, 825 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.04*, 0.09 (s, 9 H), 1.05-2.01 (m, 9 H), 5.51, 5.82* (dd, J = 6.7, 18.4, 6.5*, 18.6*, 1 H), 5.58, 5.89* (d, J = 18.4, 18.6*, 1 H); ^{13}C NMR (C_6D_6) δ -0.7 ($Si(CH_3)_3$), 21.3, 25.6*, 26.1*, 27.8 (CH_2), 25.9*, 26.4, 27.0*, 27.6 (CH), 125.5, 132.9*, 143.5*, 149.4 (CH=CH). Anal. Calcd for $C_{11}H_{20}Si$: C, 73.25; H, 11.18. Found: C, 73.34; H, 11.20.

9h. Distillation using a Kugelrohr apparatus provided 61%, showing identical and ^{13}C NMR spectra with the compound prepared from **5k** by action of *n*-BuLi.

(*E*/*Z*)-*exo*-7-(2-Bromo-1-vinyl)bicyclo[4.1.0]heptane (9j, *E*/*Z* Ratio 1:3.4*). Column chromatography, PE/ethyl acetate (4:1), supplied a pure product (51%): IR (neat) 3060, 2990, 1620, 680, 660 cm^{-1}; ^1H NMR (C_6D_6) δ 0.6-1.9 (m, 11 H), 5.11*, 5.5 (dd, J = 6.9*, 9.0*, 8.9, 13.4, 1 H), 5.70, 5.75* (d, J = 6.9*, 13.4, 1 H), ^{13}C NMR (C_6D_6) δ 21.6*, 23.2, 23.4* (CH_2), 19.6, 20.3*, 25.8*, 27.5 (CH), 100.4, 103.9*, 139.0*, 141.7 (CH=CH); MS m/z (relative intensity) 200 (M^+, 7), 134 (22), 132 (20), 121 (54). Anal. Calcd for $C_9H_{13}Br$: C, 53.75; H, 6.52; Br, 39.73. Found: C, 53.81; H, 6.42; Br, 39.43.

9i (from 5l, *E*/*Z* Ratio 5:4*). Column chromatography on silica gel using hexane provided a pure product (40%), identical with the compound described above.

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Stereoselective Convergent Synthesis of Hydroazulenes via an Intermolecular Cyclopropanation/Cope Rearrangement

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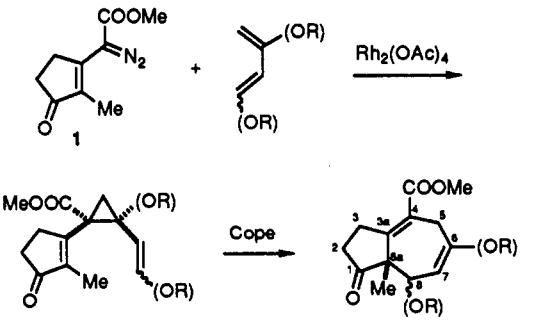
Rhodium(II) acetate catalyzed decomposition of vinyldiazomethane 1 to a vinylcarbenoid intermediate in the presence of oxygenated dienes led to the direct formation of hydroazulenes **7**, **13**, and **15-19**. The 3 + 4 annulation proceeds by a tandem cyclopropanation/Cope rearrangement sequence. The cyclopropanation is highly stereoselective, favoring the formation of *cis*-divinylcyclopropanes. Due to the boat transition state required for the Cope rearrangement of *cis*-divinylcyclopropanes, the hydroazulenes are formed with predictable stereocontrol.

The hydroazulene skeleton is an important feature of many biologically important natural products including the pseudoguaianes. Numerous synthetic strategies have been developed for the construction of this bicyclic system.[1] A particularly intriguing method, developed by Marino,[2] Wender,[3] and Piers,[4] has been the Cope rearrangement of *cis*-divinylcyclopropanes, which proceeds with predictable stereocontrol. A drawback with this approach, however, is that the isomeric *trans*-divinylcyclopropanes often undergo a competing 1,5-homodienyl rearrangement rather than equilibration to the cis isomer

Scheme I



(1) (a) Heathcock, C. H.; Grahm, S. L.; Pirrung, M. C.; Plavac, F.; White, C. T. In *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; Wiley: New York, 1983; Vol. 5, pp 333-384. (b) Rigby, J. H. In *Studies in Natural Products Chemistry*; Rahman, A., Ed.; Elsevier: New York, 1988; Vol. 1, pp 545-576. (c) Vandewalle, M.; De Clercq, P. *Tetrahedron* **1985**, *41*, 1767.

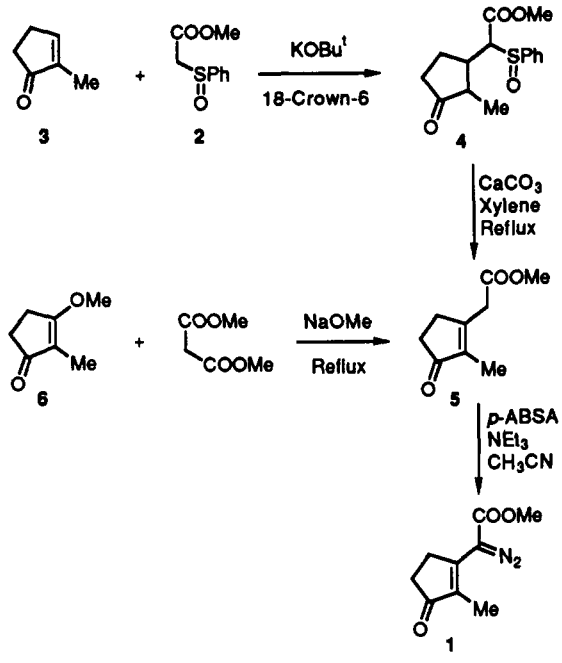
(2) (a) Marino, J. P.; Kaneko, T. *J. Org. Chem.* **1974**, *39*, 3175. (b) Marino, J. P.; Browne, L. J. *Tetradhedron Lett.* **1976**, 3245.

(3) (a) Wender, P. A.; Eissenstat, M. A.; Filosa, M. P. *J. Am. Chem. Soc.* **1979**, *101*, 2196. (b) Wender, P. A.; Filosa, M. P. *J. Org. Chem.* **1976**, *41*, 3490.

(4) (a) Piers, E.; Nagakura, I. *Tetrahedron Lett.* **1976**, 3237. (b) Piers, E.; Morton, H. E.; Nagakura, I.; Thies, R. W. *Can. J. Chem.* **1983**, *61*, 1226.

0022-3263/91/1956-0723$02.50/0

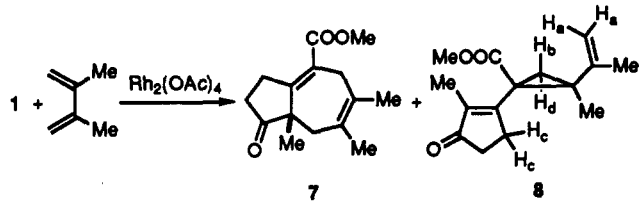
Scheme II



followed by a Cope rearrangement. Consequently, carefully controlled reaction conditions[3a] or rather elaborate stereoselective syntheses of *cis*-divinylcyclopropanes[3,4] are required.

Previous studies in our group have shown that the reaction of rhodium-stabilized vinylcarbenoids with a variety of dienes, both inter-[5] and intramolecularly,[6] is an excellent method for the stereoselective synthesis of seven-membered rings. The mechanism of this transformation has been shown to be a tandem cyclopropanation/Cope rearrangement sequence.[5b] A particular advantage of this approach over other Cope rearrangement strategies[7] is the ease in which the *cis*-divinylcyclopropane intermediate may be selectively generated. Extension of the methodology to include cyclic vinyldiazomethanes such as 1 would enable a rapid entry into the hydroazulene system to be achieved (Scheme I). Furthermore, successful reactions with 1 would demonstrate the versatility of this chemistry. Potential problems exist because the presence of the methyl group in 1 would challenge the generality of the tandem cyclopropanation/Cope rearrangement sequence. The resulting vinylcarbenoid generated from 1 may competitively rearrange by a 1,4-hydride shift[8] or, alternatively, the cyclopropanation with this more elaborate system may lack cis stereoselectivity. Also, the divinylcyclopropane, if formed, would be sterically congested and this may severely retard the Cope rearrangement of the divinylcyclopropane.[9] The synthesis of 1 and the outcome of its subsequent decomposition in the presence

Scheme III



of dienes are described in this paper.

Results

The first objective of this study was to synthesize the cyclic vinyldiazomethane 1. Reaction of the sulfoxide 2 with 2-methyl-2-cyclopentenone (3) in the presence of a catalytic amount of 18-crown-6 and potassium *tert*-butoxide generated the Michael adduct 4. Heating in xylene with 2 equiv of calcium carbonate gave the diazo precursor 5, but the overall yield was only moderate (39–43%).[10] A much more successful approach was accomplished by employing the procedure by Oberhaensli[11] (Scheme II). Thus, 3-methoxy-2-methyl-2-cyclopentenone (6) was treated with dimethyl malonate and sodium methoxide in refluxing methanol to give the diazo precursor 5 in 85% yield. Under these conditions, the Michael addition/elimination and the subsequent decarboxylation occurred in one process. Diazotization of 5 with *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) in the presence of triethylamine as base gave the desired cyclic vinyldiazomethane 1 in 92% yield. Vinyldiazomethanes with two electron-withdrawing groups are quite stable[5d] and 1 can be stored indefinitely at 10 °C.

In the presence of rhodium(II) acetate as catalyst, rapid decomposition of 1 occurred at 40 °C to generate the rhodium-stabilized vinylcarbenoid, which was then trapped by dienes. The first diene that was examined was the symmetrical 2,3-dimethyl-1,3-butadiene, and this reaction led to the formation of two products (Scheme III). The major product was the desired bicyclic system 7 (41% yield), but the *trans*-divinylcyclopropane 8 was also formed in substantial amounts (20% yield). The stereochemistry of 8 was assigned on the basis of NOE difference experiments.[12] Irradiation of the terminal vinyl protons (H_a) caused an enhancement of one cyclopropyl proton (H_b), while irradiation of the methylene protons on the cyclopentenone ring (H_c) caused enhancement of the other cyclopropyl proton (H_d). Therefore, it may be safely concluded that the *trans*-divinylcyclopropane 8 was isolated. A positive feature of this reaction is that the methyl group of the vinylcarbenoid did not cause significant problems. A 1,4-rearrangement, common in unstabilized vinylcarbenes,[8] was not observed. Steric factors did not interfere with the cyclopropanation or the Cope rearrangement but the stereoselectivity of the cyclopropanation was poor. Presumably 7 was formed from the *cis*-divinylcyclopropane while the trans isomer 8 was isolable.

The lack of stereocontrol was a concern, especially as in our previous work[5] the most striking feature of rhodium-stabilized vinylcarbenoid chemistry has been the remarkable cis stereoselectivity of the cyclopropanation step. Much greater cis stereoselectivity occurs, however, in the reaction of vinylcarbenoids with oxygenated alkenes compared with alkyl-substituted alkenes.[13] Therefore, we

(5) (a) Davies, H. M. L.; Young, W. B.; Smith, H. D. *Tetrahedron Lett.* **1989**, *30*, 4653. (b) Davies, H. M. L.; Smith, H. D.; Korkor, O. *Ibid.* **1987**, *28*, 1853. (c) Davies, H. M. L.; Clark, D. M.; Alligood, D. B. *Tetrahedron* **1987**, *43*, 4265. (d) Davies, H. M. L.; Clark, D. M.; Smith, T. K. *Tetrahedron Lett.* **1985**, *26*, 5659.

(6) (a) Davies, H. M. L.; McAfee, M. J.; Oldenburg, C. E. M. *J. Org. Chem.* **1989**, *54*, 930. (b) 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.

(7) (a) Wong, H. N. C.; Hon, M.-Y.; Tse, C.-W.; Yip, Y.-C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 165. (b) Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1.

(8) Pérez, J. D.; Yranzo, G. I. *J. Org. Chem.* **1982**, *47*, 2221.

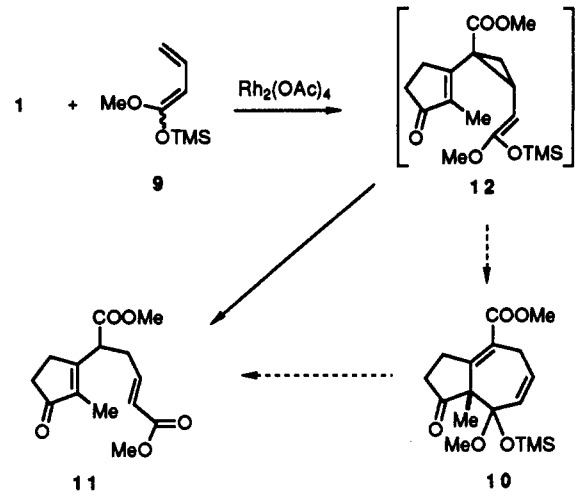
(9) (a) Schneider, M. P.; Rau, A. *J. Am. Chem. Soc.* **1979**, *101*, 4426. (b) Sasaki, T.; Eguchi, S.; Ohno, M. *J. Org. Chem.* **1972**, *37*, 466.

(10) Takasu, M.; Wakabayashi, H.; Furuta, K.; Yamamoto, H. *Tetrahedron Lett.* **1988**, *29*, 6943.

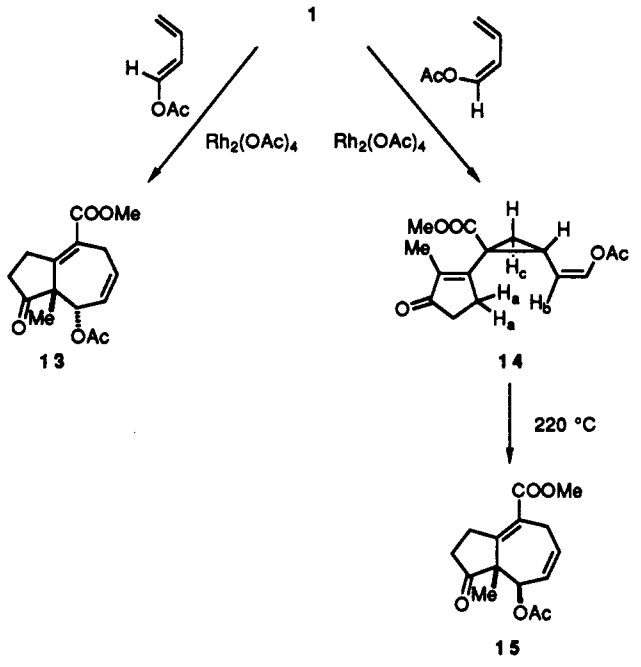
(11) Oberhaensli, P. (L. Givaudan, L., et Cie, S. A.) Ger. Offen. 2,008,833, 24 Sep 1970; *Chem. Abstr.* **1970**, *73*, 109364e.

(12) Details of NOE data are supplied in the supplementary material.

Scheme IV



Scheme V

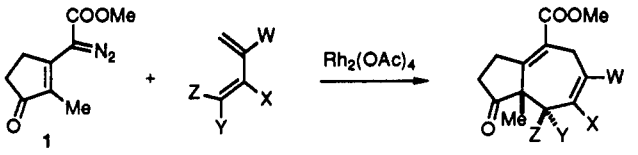


expected 1-methoxy-1-[(trimethylsilyl)oxy]-1,3-butadiene (**9**) to be more effective in its reaction with **1** than 2,3-dimethyl-1,3-butadiene. Decomposition of **1** in the presence of **9**, however, failed to generate any of the 5,7-fused product **10**. Instead, an apparent alkylation product (**11**) was isolated in 41% yield (Scheme IV). The formation of **11** may be rationalized by assuming that the introduction of functionality at the diene terminus resulted in a very crowded divinylcyclopropane intermediate (**12**). The Cope rearrangement of **12** would be inhibited by these steric constraints, and hydrolysis of the silyl group occurred instead with concomitant ring opening of the cyclopropane to form the alkylation product **11**. An alternative mechanistic possibility would be that the 5,7-fused product **10** was unstable and underwent hydrolysis and a retro-Claisen condensation to form **11**.

Confirmation of the importance of steric factors in the Cope rearrangement was obtained from the reactions with the geometrically defined *trans*- and *cis*-1-acetoxy-1,3-butadienes. Decomposition of **1** in the presence of

(13) Davies, H. M. L.; Clark, T. J.; Church, L. A. *Tetrahedron Lett.* **1989**, *30*, 5057.

Table I. Synthesis of Hydroazulenes via Reaction of 1 with Dienes



entry	W	X	Y	Z	product	yield, %
1	Me	Me	H	H	7	41[a]
2	H	H	OAc	H	13	67
3	H	H	H	OAc	15	62[b]
4	H	H	OTMS	H	16	86
5	OTMS	H	H	H	17	53
6	OTBDMS	H	H	H	18	94
7	OTMS	H	OMe	H	19	59

[a] 20% of **8** was also formed. [b] Overall yield for cyclopropanation followed by heating at 220 °C.

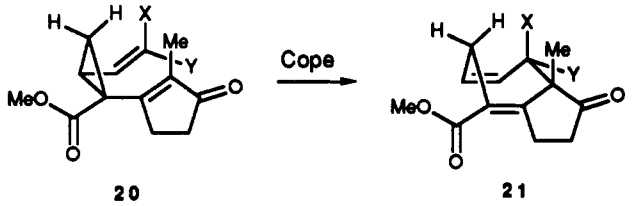
trans-1-acetoxy-1,3-butadiene led cleanly to the formation of the trans hydroazulene **13** in 67% yield (Scheme V). Furthermore, there was no evidence of a *trans*-divinylcyclopropane in the proton NMR of the crude reaction mixture, which suggests that the cyclopropanation was highly stereoselective. In contrast, decomposition of **1** in the presence of *cis*-1-acetoxy-1,3-butadiene did not generate directly a hydroazulene product. Instead, the *cis*-divinylcyclopropane **14** was isolated in 80% yield. The cis arrangement in **14** was readily determined by NOE difference spectroscopy, in which a distinctive enhancement of both H_b and H_c was observed upon irradiation of H_a.[12] The *cis*-divinylcyclopropane **14** was stable at ambient temperatures, but on heating at 220 °C under argon for 30 min, rearrangement occurred to give the cis hydroazulene **15** in 73% yield. Assignment of the cis and trans configurations to the hydroazulenes was based on the magnitude of the NOE enhancement of the adjacent proton at C-8 compared to the enhancement of the C-7 vinyl proton upon irradiation of the C-8a methyl group. For the trans isomer **13**, a large enhancement (11%, 7 times the enhanement of the C-7 proton) was observed, while for the cis isomer **15**, the enhancement was considerably smaller (2%, 1 times the enhancement of the C-7 proton).[12]

Several (silyloxy)butadienes were also reacted with the cyclic vinyldiazomethane **1** and the results are shown in Table I (entries 4–7). Very high yields were observed in certain cases, which presumably is due to the diminished likelihood of interfering reactions at the silyloxy group compared to the acetoxy group. Decomposition of **1** in the presence of *trans*-1-[(trimethylsilyl)oxy]-1,3-butadiene gave a very clean reaction, leading to the formation of the trans cycloadduct **16** in 86% yield. The formation of a series of hydroazulenes with oxygen functionality at C-8 may be very useful for the eventual synthesis of certain ambrosanolides.[1a] Internally substituted dienes were also examined in order to determine whether oxygen functionality could be introduced at C-6, which could possibly lead to confertin[14] and damsin.[15] With 2-[(trimethylsilyl)oxy]-1,3-butadiene, the desired regiochemistry was observed, but the resulting bicyclic system **17** was isolated in rather moderate yield (53%). By use of the more robust *tert*-butyldimethylsilyl group, however, the yield of the bicyclic system **18** was improved to 94%. Finally, reaction of **1**

(14) Heathcock, C. H.; DelMar, E. G.; Graham, S. L. *J. Am. Chem. Soc.* **1982**, *104*, 1907.

(15) (a) Roberts, M. R.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1979**, *101*, 7626. (b) Quallich, G. J.; Schlessinger, R. H. *Ibid.* **1979**, *101*, 7627.

Scheme VI



with Danishefsky's diene was also effective and gave the cycloadduct **19** in 59% yield as the trans isomer. Hydrolysis of **19** could not be accomplished without induction of a retro-Michael addition.

Discussion

The successful utilization of the vinyldiazomethane **1** for the tandem cyclopropanation/Cope rearrangement sequence illustrates that considerable variation is possible with this chemistry. Neither the ring structure nor the methyl group caused serious problems. Effective cyclopropanations occurred, and even though poor stereoselectivity was observed in the reaction of **1** with 2,3-dimethyl-1,3-butadiene (2:1), the reactions with oxygenated dienes were remarkably stereoselective with no evidence for *trans*-divinylcyclopropanes. The regiochemistry of the cyclopropanation is as expected and follows the trends observed with ethyl diazoacetate.[16] In the case of 1-substituted dienes, reaction occurs at the least hindered double bond, while with the 2-substituted dienes, the more electron-rich double bond is favored.

The stereochemistry of the hydroazulenes can be rationalized by considering the transition state for the Cope rearrangement of divinylcyclopropanes, as illustrated in Scheme VI. Rearrangement occurs through the boat transition state **20** in which the vinyl groups point toward the cyclopropane ring.[17] In this way, the initial diene geometry dictates the stereochemistry of the product **21**. A trans diene substituent (Y) would generate a trans hydroazulene, while a cis substituent (X) would lead to a cis product. Furthermore, it is also apparent that a cis substituent could exert a much greater steric crowding in the transition state than a trans substituent.[9] This effect was manifested in the case of *cis*-acetoxybutadiene where the *cis*-divinylcyclopropane was isolable and required vigorous conditions to undergo the subsequent Cope rearrangement.

In summary, the cyclopropanation/Cope rearrangement sequence was shown to be a viable method for the synthesis of hydroazulenes. The annulations proceeded in good to excellent yields with predictable control of relative stereochemistry. Once again, remarkable selectivity for the formation of *cis*-divinylcyclopropane intermediates was observed, even though a complex and bulky vinylcarbenoid precursor (**1**) was used. Efforts are underway to extend this methodology to the enantioselective syntheses of pseudoguaianes.

Experimental Section

Dichloromethane was distilled over calcium hydride. Tetrahydrofuran (THF) was distilled over sodium benzophenone ketyl. Methanol was dried over 4-Å molecular sieves. ^1H and ^{13}C NMR spectra were recorded at 200 and 50.3 MHz, respectively. Mass spectral determinations were carried out at 70 eV. *cis*-1-Acetoxy-1,3-butadiene,[18] *trans*-1-acetoxy-1,3-butadiene,[19] 1-methoxy-1-[(trimethylsilyl)oxy]-1,3-butadiene,[21] *trans*-1-[(trimethylsilyl)oxy]-1,3-butadiene,[21] 2-[(trimethylsilyl)oxy]-1,3-butadiene,[21] and 2-[(*tert*-butyldimethylsilyl)oxy]-1,3-butadiene[22] were prepared from literature procedures or variations thereof. 2,3-Dimethyl-1,3-butadiene and *trans*-1-methoxy-3-[(trimethylsilyl)oxy]-1,3-butadiene were purchased from Aldrich Chemical Co. and were used without further purification. Methyl (phenylsulfinyl)acetate (**2**)[23] was prepared by sodium perborate oxidation of methyl (phenylthio)acetate according to the procedure of McKillop.[24]

Methyl 2-Methyl-3-oxo-1-cyclopentene-1-acetate (5).[11] With use of the general procedure of Yamamoto et al.,[10] a mixture of 18-crown-6 (6.26 g, 23.7 mmol) and potassium *tert*-butoxide (2.04 g, 18.2 mmol) in dry THF (15 mL) was stirred for 15 min under argon at room temperature and then cooled to −78 °C. A solution of **2** (12.04 g, 60.8 mmol) in THF was added dropwise, and the mixture was allowed to stir for 15 min. A solution of 2-methyl-2-cyclopentenone (**3**) (5.84 g, 60.8 mmol) in THF was added, and the mixture was stirred for 1 h at −78 °C, warmed to room temperature, and then stirred for 48 h. The reaction was quenched with saturated NaCl/dilute HCl and extracted with CH_2Cl_2 (3×). The organic phase was washed with aqueous NaCl, dried ($MgSO_4$), and concentrated under vacuum. The residue was combined with $CaCO_3$ (7.00 g, 120 mmol) and xylene (200 mL), and the mixture was heated to reflux for 24 h. The mixture was cooled, vacuum filtered, and concentrated under vacuum. Purification of the residue by silica gel column chromatography (1/1 ether/petroleum ether, R_f 0.33) gave **5** as a yellow oil (4.37 g, 43%): IR (neat) 3005, 2970, 2935, 2870, 1730, 1690, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.69 (s, 3 H), 3.41 (s, 2 H), 2.62–2.52 (m, 2 H), 2.41–2.35 (m, 2 H), 1.69 (t, 3 H, J = 2.1 Hz); ^{13}C NMR ($CDCl_3$) δ 209.1, 169.3, 163.3, 138.8, 52.1, 36.5, 34.0, 29.7, 8.0. Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.35; H, 7.20. With use of the general procedure of Oberhaensli,[11] sodium metal (3.08 g, 134 mmol) was washed with pentane and added slowly with stirring to dry methanol (250 mL). After the sodium dissolved, dimethyl malonate (16.24 g, 123 mmol) was added, and the mixture was stirred for 15 min. 3-Methoxy-2-methyl-2-cyclopentenone[25] (**6**) (14.10 g, 112 mmol) in a solution of methanol (50 mL) was added, and the mixture was heated under reflux for 48 h. The mixture was cooled to 0 °C, and concentrated HCl was added until the pH was 7. The methanol was then removed under vacuum. Aqueous NaCl was added to the residue, and the mixture was extracted with ether (2×). The organic layer was dried ($MgSO_4$) and concentrated under vacuum. Purification of the residue by short-path distillation (80–118 °C, 0.3 mmHg) gave **5** as a colorless oil (15.96 g, 85%).

Methyl α-Diazo-2-methyl-3-oxo-1-cyclopentene-1-acetate (1). Triethylamine (2.71 g, 26.8 mmol) was added rapidly to a stirred mixture of **5** (1.50 g, 8.93 mmol) and *p*-acetamidobenzenesulfonyl azide[26] (2.25 g, 9.38 mmol) in acetonitrile (50 mL) at 0 °C. The mixture was warmed to room temperature and then stirred for 12 h. The solvent was removed under vacuum, and the residue was triturated with a mixture of 1/1 ether/petroleum ether (100 mL). The mixture was vacuum filtered, the precipitate was washed with a mixture of 1/1 ether/petroleum ether (100 mL), and the filtrate and wash were combined and concentrated under vacuum to give the crude product. Purification by silica gel column chromatography (1/1 ether/petroleum ether, R_f 0.23) gave **1** as orange crystals (mp 61–63 °C, 1.59 g, 92%); IR ($CHCl_3$) 3010, 2960, 2930, 2860, 2105, 1680, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.82 (s, 3 H), 2.91–2.83 (m, 2 H), 2.44–2.38 (m, 2 H), 1.78 (t, 3 H, J = 2.1 Hz); ^{13}C NMR ($CDCl_3$) δ 206.9, 163.5, 153.3, 130.6, 64.8, 52.3, 33.4, 28.3, 8.3. Anal. Calcd for $C_9H_{10}N_2O_3$: C, 55.67; H, 5.19; N, 14.43. Found: C, 55.80; H, 5.23; N, 14.39.

General Procedure for the Decomposition of 1 with Dienes

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in the Presence of Rhodium(II) Acetate. A solution of 1 (1 equiv) in dry CH_2Cl_2 was added dropwise to a refluxing mixture of the diene (5 equiv) and rhodium(II) acetate dimer (0.01 equiv) in dry CH_2Cl_2 under an argon atmosphere. After the addition was complete, the mixture was refluxed for an additional 30 min. The mixture was then cooled and concentrated under vacuum to yield the crude product.

Methyl 1,2,3,5,8,8a-Hexahydro-1-oxo-6,7,8a-trimethyl-4-azulenecarboxylate (7) and Methyl 1β-Methyl-1α-(2-propenyl)-2β-[1-(2-methyl-3-oxo-1-cyclopentenyl)]-2α-cyclopropanecarboxylate (8). The reaction was carried out on a 2.58-mmol scale with 2,3-dimethyl-1,3-butadiene. Purification by silica gel column chromatography (1/4 ether/petroleum ether) gave two products. **7** (0.26 g, 41%): colorless oil, R_f 0.50; IR (neat) 2950, 2920, 2860, 1740, 1705, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.75 (s, 3 H), 3.17 (br d, 1 H, J = 16.1 Hz), 2.91 (br d, 1 H, J = 16.1 Hz), 3.14–2.70 (m, 2 H), 2.58 (ddd, 1 H, J = 19.0, 10.3, 3.4 Hz), 2.49 (d, 1 H, J = 15.4 Hz), 2.25 (d, 1 H, J = 15.4 Hz), 2.20 (ddd, 1 H, J = 19.0, 10.0, 8.8 Hz), 1.73 (s, 3 H), 1.70 (s, 3 H), 1.13 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 218.1, 168.8, 154.5, 130.5, 126.7, 126.2, 52.1, 51.3, 38.1, 34.6, 34.4, 26.4, 22.8, 21.6, 20.7. Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.37; H, 8.17.

8 (0.13 g, 20%): colorless oil, R_f 0.27; IR (neat) 3070, 2940, 2910, 2855, 1720, 1690, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.96 (s, 1 H), 4.92 (s, 1 H), 3.60 (s, 3 H), 2.78 (br d, 1 H, J = 18.8 Hz), 2.49 (br d, 1 H, J = 18.8 Hz), 2.45–2.38 (m, 2 H), 2.11 (d, 1 H, J = 5.2 Hz), 1.80 (t, 3 H, J = 2.4 Hz), 1.75 (s, 3 H), 1.16 (s, 3 H), 1.10 (d, 1 H, J = 5.2 Hz); ^{13}C NMR ($CDCl_3$) δ 210.2, 169.7, 166.6, 144.5, 141.7, 113.7, 52.0, 38.6, 36.5, 34.1, 30.3, 25.2, 22.2, 20.5, 9.4; MS m/z (rel intensity) 248 (22), 233 (90), 217 (10), 201 (22), 189 (100), 173 (50), 159 (22), 147 (65), 133 (20), 117 (28), 105 (26), 91 (38), 77 (25); HRMS calcd for $C_{15}H_{20}O_3$ 248.1413, found 248.1407.

Methyl 5-(2-Methyl-3-oxo-1-cyclopent-1-enyl)-5-(methoxycarbonyl)-2-pentenoate (11). The reaction was carried out on a 2.58-mmol scale with 1-methoxy-1-[(trimethylsilyl)oxy]-1,3-butadiene. Purification by silica gel column chromatography (1/1 ether/petroleum ether, R_f 0.17) gave **11** as a colorless oil (0.28 g, 41%): IR (neat) 3030, 2970, 2930, 2860, 1725, 1700, 1645 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.78 (dt, 1 H, J = 15.7, 7.2 Hz), 5.85 (dt, 1 H, J = 15.7, 1.4 Hz), 3.83 (t, 1 H, J = 7.3 Hz), 3.70 (s, 6 H), 2.96–2.79 (m, 1 H), 2.62–2.46 (m, 1 H), 2.52–2.43 (m, 2 H), 2.40–2.34 (m, 2 H), 1.72 (t, 3 H, J = 2.1 Hz); ^{13}C NMR ($CDCl_3$) δ 208.3, 170.4, 165.6, 165.2, 143.8, 138.6, 122.9, 51.9, 50.9, 45.2, 33.3, 31.6, 26.0, 7.7. Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.24; H, 6.86.

Methyl 1,2,3,5,8,8a-Hexahydro-8α-acetoxy-8aβ-methyl-1-oxo-4-azulenecarboxylate (13). The reaction was carried out on a 2.58-mmol scale with *trans*-1-acetoxy-1,3-butadiene. Purification by silica gel column chromatography (3/7 ether/petroleum ether, R_f 0.35) gave **13** as a colorless oil (0.48 g, 67%): IR ($CHCl_3$) 3040, 2970, 2950, 2890, 1740, 1710, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.93–5.85 (m 2 H), 5.29 (br d, 1 H, J = 4.4 Hz), 3.75 (s, 3 H), 3.51 (dd, 1 H, J = 21.7, 6.4 Hz), 3.18 (br d, 1 H, J = 21.7 Hz), 3.20–3.04 (m, 2 H), 2.64–2.28 (m, 2 H), 1.89 (s, 3 H), 1.21 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 218.7, 169.5, 168.0, 155.3, 131.9, 125.2, 123.6, 74.0, 55.5, 51.6, 35.9, 30.1, 27.9, 20.7, 18.5. Anal. Calcd for $C_{15}H_{18}O_5$: C, 64.74; H, 6.52. Found: C, 64.64; H, 6.54.

Methyl 1β-(*cis*-2-Acetoxyethenyl)-2β-[1-(2-methyl-3-oxo-1-cyclopentenyl)]-2α-cyclopropanecarboxylate (14). The reaction was carried out on a 6.13-mmol scale with *cis*-1-acetoxy-1,3-butadiene. Purification by silica gel column chromatography (2/3 ether/petroleum ether, R_f 0.15) gave **14** as a white solid (mp 93–95 °C, 1.36 g, 80%): IR ($CHCl_3$) 3020, 2960, 2925, 1755, 1720, 1695, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.11 (d, 1 H, J = 6.5 Hz), 4.12 (dd, 1 H, J = 10.2, 6.5 Hz), 3.69 (s, 3 H), 2.91 (dt, 1 H, J = 9.8, 6.8 Hz), 2.56–2.50 (m, 2 H), 2.42–2.38 (m, 2 H), 2.17 (s, 3 H), 1.90 (dd, 1 H, J = 9.2, 4.6 Hz), 1.66 (t, 3 H, J = 2.0 Hz), 1.21 (dd, 1 H, J = 6.8, 4.6 Hz); ^{13}C NMR ($CDCl_3$) δ 210.0, 171.7, 167.5, 164.7, 142.3, 136.8, 110.5, 52.7, 34.3, 31.0, 29.7, 24.7, 22.2, 20.6, 9.1; MS m/z (rel intensity) 278 (11), 236 (57), 205 (17), 168 (76), 137 (19), 110 (22), 91 (16), 77 (14), 55 (11), 43 (100); HRMS calcd for $C_{15}H_{18}O_5$ 278.1154, found 278.1147. Anal. Calcd for $C_{15}H_{18}O_5$: C, 64.74; H, 6.52. Found: C, 64.81; H, 6.57.

Methyl 1,2,3,5,8,8a-Hexahydro-8β-acetoxy-8aβ-methyl-1-oxo-4-azulenecarboxylate (15). A portion of **14** (0.74 g, 2.66 mmol) was placed in a Pyrex test tube with a magnetic stir bar and rubber septum under a flow of argon. The tube was immersed in an oil bath at 220 °C and stirred for 30 min. Purification by silica gel column chromatography (1/1 ether/petroleum ether, R_f 0.50) gave **15** as a white solid (mp 91–93 °C, 0.54 g, 73%): IR ($CHCl_3$) 3030, 2960, 2860, 1740, 1705, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.75–5.58 (m, 2 H), 5.34 (br d, 1 H, J = 12.0 Hz), 3.75 (s, 3 H), 3.57–2.29 (m, 6 H), 2.04 (s, 3 H), 1.30 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 215.9, 170.4, 168.1, 154.0, 128.4, 127.4, 126.9, 67.7, 55.7, 51.8, 35.8, 28.8, 27.8, 20.9, 13.1; MS m/z (rel intensity) 278 (13), 236 (82), 204 (20), 168 (95), 131 (22), 105 (18), 83 (71), 43 (100); HRMS calcd for $C_{15}H_{18}O_5$ 278.1154, found 278.1147. Anal. Calcd for $C_{15}H_{18}O_5$: C, 64.74; H, 6.52. Found: C, 64.62; H, 6.55.

Methyl 1,2,3,5,8,8a-Hexahydro-8aβ-methyl-1-oxo-8α-[(trimethylsilyl)oxy]-4-azulenecarboxylate (16). The reaction was carried out on a 2.58-mmol scale with *trans*-1-[(trimethylsilyl)oxy]-1,3-butadiene. Purification by silica gel column chromatography (1/5 ether/petroleum ether, R_f 0.51) gave **16** as a colorless oil (0.68 g, 86%): IR (neat) 3020, 2960, 2900, 2880, 1740, 1705, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.83–5.58 (m, 2 H), 4.26 (dd, 1 H, J = 6.3, 1.9 Hz), 3.75 (s, 3 H), 3.59–2.87 (m, 4 H), 2.48–2.33 (m, 2 H), 1.16 (s, 3 H), 0.02 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 219.9, 167.4, 157.7, 129.0, 127.1, 124.4, 72.5, 57.7, 50.9, 36.4, 29.2, 27.9, 16.9, −0.2. Anal. Calcd for $C_{16}H_{24}O_4Si$: C, 62.30; H, 7.84. Found: C, 62.21; H, 7.87.

Methyl 1,2,3,5,8,8a-Hexahydro-8a-methyl-1-oxo-6-[(trimethylsilyl)oxy]-4-azulenecarboxylate (17). The reaction was carried out on a 2.58-mmol scale with 2-[(trimethylsilyl)oxy]-1,3-butadiene. Purification by silica gel column chromatography (3/7 ether/petroleum ether, R_f 0.35) gave **17** as a colorless oil (0.42 g, 53%): IR ($CHCl_3$) 3030, 2960, 2910, 2850, 1735, 1705, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.93 (dd, 1 H, J = 7.0, 4.2 Hz), 3.75 (s, 3 H), 3.42 (br d, 1 H, J = 21.0 Hz), 3.16 (br d, 1 H, J = 21.0 Hz), 3.20–2.85 (m, 2 H), 2.55 (ddd, 1 H, J = 18.7, 9.9, 5.8 Hz), 2.37 (ddd, 1 H, J = 18.7, 9.9, 8.2 Hz), 2.21–2.13 (m, 2 H), 1.24 (s, 3 H), 0.19 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 207.6, 168.4, 157.2, 148.6, 122.7, 103.3, 52.0, 51.6, 35.2, 30.6, 27.3, 20.0, 17.3, 0.2. Anal. Calcd for $C_{16}H_{24}O_4Si$: C, 62.30; H, 7.84. Found: C, 62.17; H, 7.80.

Methyl 1,2,3,5,8,8a-Hexahydro-6-[(*tert*-butyldimethylsilyl)oxy]-8a-methyl-1-oxo-4-azulenecarboxylate (18). The reaction was carried out on a 2.72-mmol scale with 2-[(*tert*-butyldimethylsilyl)oxy]-1,3-butadiene. Purification by silica gel column chromatography (1/4 ether/petroleum ether, R_f 0.45) gave **18** as a colorless oil (0.89 g, 94%): IR ($CHCl_3$) 2950, 2925, 2885, 2850, 1735, 1705, 1670, 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.90 (dd, 1 H, J = 7.2, 4.1 Hz), 3.74 (s, 3 H), 3.40 (br d, 1 H, J = 18.9 Hz), 3.23–2.84 (m, 3 H), 2.52 (ddd, 1 H, J = 18.9, 9.9, 5.8 Hz), 2.34 (ddd, 1 H, J = 18.9, 10.3, 8.5 Hz), 2.20–2.11 (m, 2 H), 1.25 (s, 3 H), 0.90 (s, 9 H), 0.11 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 219.8, 168.3, 157.1, 148.8, 122.7, 102.9, 51.9, 51.5, 34.9, 34.8, 30.6, 27.2, 25.5, 20.0, 17.8, −4.6. Anal. Calcd for $C_{19}H_{30}O_4Si$: C, 65.10; H, 8.63. Found: C, 64.97; H, 8.68.

Methyl 1,2,3,5,8,8a-Hexahydro-8α-methoxy-8aβ-methyl-6-[(trimethylsilyl)oxy]-1-oxo-4-azulenecarboxylate (19). The reaction was carried out on a 1.05-mmol scale with *trans*-1-methoxy-3-[(trimethylsilyl)oxy]-1,3-butadiene. Purification by silica gel column chromatography (1/1 ether/petroleum ether, R_f 0.6) gave **19** as a colorless oil (0.21 g, 59%): IR (neat) 2950, 2810, 1740, 1705, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.10 (d, 1 H, J = 7.4 Hz), 3.78 (d, 1 H, J = 7.4 Hz), 3.65 (s, 3 H), 3.46 (d, 1 H, J = 21.7 Hz), 3.16–2.80 (m, 3 H), 3.09 (s, 3 H), 2.40–2.30 (m, 2 H), 1.02 (s, 3 H), 0.13 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 219.7, 167.5, 157.0, 153.4, 121.2, 102.9, 79.9, 56.4, 55.9, 51.1, 35.9, 35.7, 27.9, 18.4, −0.1; MS m/z (rel intensity) 338 (12), 323 (5), 306 (18), 279 (35), 263 (15), 234 (55), 205 (16), 178 (28), 146 (22), 121 (20), 91 (48), 73 (100); HRMS calcd for $C_{17}H_{26}O_5Si$ 338.1549, found 338.1560.

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Supplementary Material Available: NOE data for compounds **8**, **13–16**, and **19** (4 pages). Ordering information is given on any current masthead page.