(73%) of 6S diol 3 (ee = 87%) at pH 7. The same experiments were carried out without fungus at pH 2 and pH 7. At pH 7, (6S)-2 and (6R)-2 epoxides were not hydrolyzed after 20 h of stirring. At pH 2, the hydrolysis of (6S)-2 epoxide yielded 26 mg (81%) of (6S)-3 diol (ee = 92%) and (6R)-2 epoxide yielded 25 mg (78%) of (6R)-3 diol (ee = 93%). It should be noted that the epoxides 2 were completely hydrolyzed after only a few minutes of stirring.

Acknowledgment. We acknowledge the Museum d'Histoire Naturelle (Paris) for its gift of the *Aspergillus niger* strain (LCP 521), the Service Central d'Analyse of the CNRS (Vernaison, France) for the mass spectral analysis, Dr. J.C. Promé (Toulouse, France) for his assistance in the mass spectral interpretation, and the Société Roquette S. A. (Lille, France) for the gift of corn-steep liquor samples.

Registry No. 1, 57706-89-5; 2, 132541-28-7; 3 (6R), 122313-83-1; 3 (6S), 122313-77-3; geraniol, 106-24-1; geraniol-6(S),7-diol, 63955-78-2; geraniol-6(R),7-diol, 63955-79-3.

Stereoselective Synthesis of Seven-Membered Carbocycles by a Tandem Cyclopropanation/Cope Rearrangement between Rhodium(II)-Stabilized Vinylcarbenoids and Dienes

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Rhodium(II)-catalyzed decomposition of vinyldiazomethanes in the presence of dienes generated 1,4-cycloheptadienes by a tandem cyclopropanation/Cope rearrangement. Excellent stereocontrol of up to three stereogenic centers in the cycloheptadienes was achieved. The stereoselectivity of the initial cyclopropanation ranged from 4:1 to >20:1, favoring *cis*-divinylcyclopropanes, and good regiocontrol was observed in the cyclopropanation of unsymmetrical dienes. Unless sterically encumbered, the *cis*-divinylcyclopropanes rearranged cleanly to cycloheptadienes under the reaction conditions. The *trans*-divinylcyclopropanes, when formed, were sufficiently stable to be observed in the crude reaction mixtures, but most were prone to facile 1,5-homodienyl rearrangements.

General synthetic processes to seven-membered carbocycles are very valuable because these rings are present in several important classes of natural products.[1] In recent years several useful annulation protocols to this ring size have been developed. The 3 + 4 cycloaddition between dienes and allyl or iron oxyallyl cations has been widely used,[2,3] while related approaches have been reported by Trost[4] and Molander.[5] The recently discovered concerted $4\pi + 2\pi$ cycloaddition between a nucleophilic vinylcarbene and electron-deficient cyclic dienes is another intriguing approach.[6] Other methods based on 5 + 2 annulations have also been described.[7]

Table I. Synthesis and Rhodium(II) Acetate Catalyzed Decomposition of 2 in the Presence of Cyclopentadiene as Outlined in Eq 2

substrate	R^1	R^2	R^3	2 (% yield)	product (% yield)
1a	COOEt	COOEt	H	**2a** (87)	**3a** (98)
1b	COOEt	CH=CHPh	H	**2b** (56)	**3b** (72)
1c	COOEt	SO_2Ph	H	**2c** (24)	**3c** (80)
1d	COOMe	Ph	H	**2d** (89)	**3d** (73)
1e	COMe	Ph	H	**2e** (66)	**3e** (66)
1f	COOEt	COOEt	OEt	**2f** (86)	**4** (77)

We have been engaged in a program to develop an alternative strategy for the synthesis of seven-membered rings through a tandem cyclopropanation/Cope rearrangement sequence between rhodium(II)-stabilized vinylcarbenoids[8,9] and dienes as illustrated in eq 1.[10,11] The Cope rearrangement of divinylcyclopropanes has been extensively used for the synthesis of seven-membered

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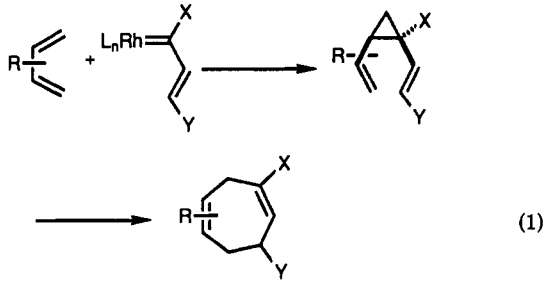
rings.[12] Excellent stereocontrol is possible because the rearrangement is stereospecific, proceeding through a boat transition state. An efficient cyclopropanation between vinylcarbenoids and dienes could alleviate the synthetic problems often associated with the synthesis of complex divinylcyclopropanes. Considering that chiral catalysts[13] or chiral auxiliaries[14] on simple carbenoids can lead to effective asymmetric cyclopropanations, the proposed process could eventually lead to the enantioselective synthesis of seven-membered carbocycles.

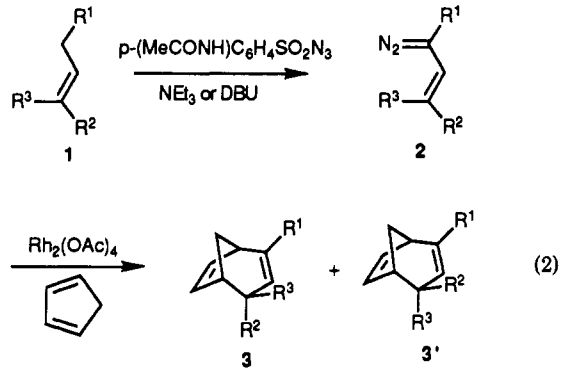


(1)

Normally, intermolecular cyclopropanations with metal-stabilized carbenoids are not particularly stereoselective.[15] Even though, in principle, cycloheptadienes could be formed from both the *cis*- and *trans*-divinylcyclopropanes, much milder reaction conditions would be possible and the likelihood of competing side reactions would be decreased if cis isomers were cleanly formed in the cyclopropanation step. In contrast to simple carbenoids, the initial cyclopropanation by vinylcarbenoids of furans,[10a,b] pyrroles[10c] and cyclopentadiene[10d] was remarkably stereoselective with no evidence for the formation of *trans*-divinylcyclopropanes or products derived from them. In this paper we define both the regio- and stereoselectivity of the reaction of vinylcarbenoids with dienes.

Results

At the onset of this study, we required vinyldiazomethanes of reasonable stability as vinylcarbenoid precursors. Vinyldiazomethanes have been used in several synthetic schemes[16] including the synthesis of divinylcyclopropanes and as precursors of metal-stabilized vinylcarbenoids, but in general, they tend to be rather labile and readily cyclize to 3*H*-pyrazoles.[17] From kinetic studies on this electrocyclization,[17a,b] it would appear that introduction of electron-withdrawing groups onto the vinyldiazomethane stabilizes the system. Therefore, vinyldiazomethanes with two electron-withdrawing groups were considered to be promising substrates for this study. These were prepared by a diazo-transfer reaction using *p*-acetamidobenzenesulfonyl azide[18] (eq 2, Table I).[19] With **1a** and **1c**, triethylamine was an effective base, but with the less acidic systems **1b,d–f**, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was required. The stability of vinyldiazomethane **2a** has been described previously.[10a] The other derivatives also have reasonable stability at 0 °C in solution, but some decomposition was apparent after a few days at room temperature. In the unsymmetrical systems **1b,d–f**, clean diazotization α to the carbonyl was observed, but with **1c**, a trace of the regioisomer **2c** was also formed, which was readily removed by chromatography. The *E* geometry for **2a–e** was readily apparent from the coupling constants of the vinyl protons while the *Z* geometry for **2f** was assigned on the basis of the chemical shift for the vinyl proton.



(2)

Prior to our studies, intermolecular cyclopropanations with metal-stabilized vinylcarbenoids had resulted in poor yields (6–40%) and stereoselectivity (cis:trans, 2:1 to 1.2:1).[16e-g] Consequently, the formation of the bicyclic structure **3a** in 98% yield from the rhodium(II) acetate catalyzed decomposition of **2a** in the presence of cyclopentadiene was very gratifying.[10d] Similar results were obtained with **2b–e**, which demonstrated that a range of electron-withdrawing groups on the vinylcarbenoid were tolerated. The stereochemistry of the bicyclic structures **3** was readily assigned by the distinctive coupling constant to the bridgehead.[10a,d,20] In the endo isomer, the coupling was ~5 Hz while no coupling to the bridgehead was observed for the exo isomer. In the case of **3a,b,d,e**, proton NMR spectra of the crude reaction mixtures showed that the endo isomers were exclusively formed, but due to the very acidic proton in **3a**, partial isomerization to the exo isomer **3a′** occurred during its attempted chromatographic purification. The isomerization was more pronounced with **3c**, as partial isomerization to the exo isomer **3c′** was evident even in the crude reaction mixture.

In the case of the more sterically congested vinyldiazomethane **2f**, the [3.2.1]bicyclic system **3f** was not formed directly.[10d] Instead, the *cis*-divinylcyclopropane **4** was isolated in 74% yield (eq 3). The stereochemistry of **4** was readily determined through NOE difference analysis, which showed strong enhancements between the vinyl protons.[21] On prolonged standing, **4** slowly rearranged to the bicyclic system **3f**, and on heating in toluene for 12 h,

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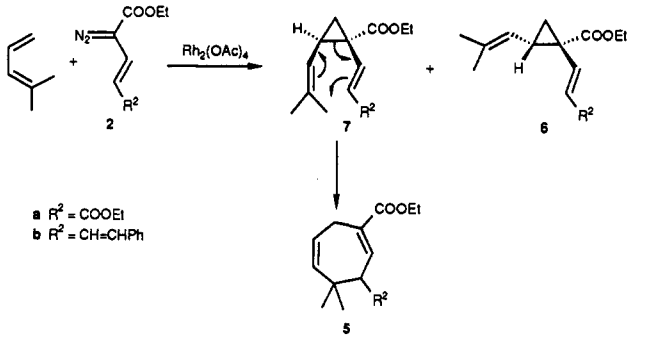
(21) Complete data of the NOE difference experiments are given in the supplementary material.

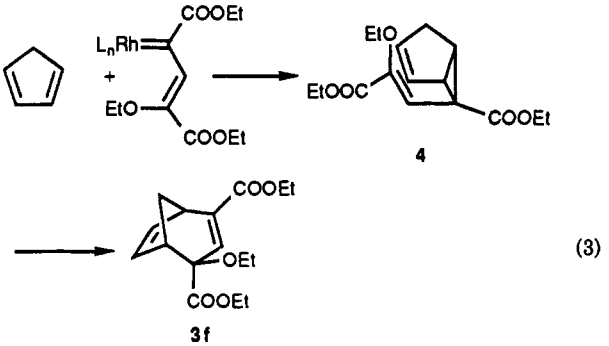
Table II. Rhodium(II) Catalyzed Decomposition of 2 in the Presence of Acyclic Dienes

diene	substrate	products (% yield)
4-methyl-1,3-pentadiene	**2a**	**5a** (58), **6a** (14)
4-methyl-1,3-pentadiene	**2b**	**5b** (80)
2,4-dimethyl-1,3-pentadiene	**2a**	**8a** (63) **10a** (14)
2,4-dimethyl-1,3-pentadiene	**2b**	**8b** (59)
2,3-dimethyl-1,3-butadiene	**2a**	**11a** (49), **12a** (13)
2,3-dimethyl-1,3-butadiene	**2b**	**11b** (42)
trans-1,3-pentadiene	**2b**	**13a** (75)
cis-1,3-pentadiene	**2b**	**13b** (68)
cis,trans-2,4-hexadiene	**2b**	**13c** (53)
2-methyl-1,3-butadiene	**2b**	**11d,e** (72, 6:1 ratio)
1-acetoxy-1,3-butadiene	**2a**	**15a** (50)
1-acetoxy-1,3-butadiene	**2c**	**15c** (67)

Scheme I



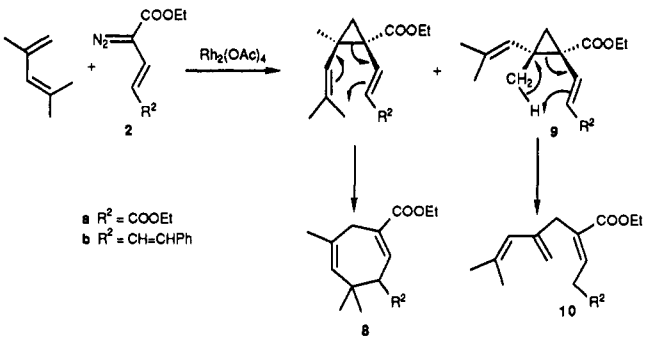
this transformation was achieved in essentially quantitative yield.[10d] Due to the substitution pattern, stereochemical determination of **3f** based on coupling constants was not possible. Instead, the tentative assignment for **3f** was based on chemical shifts for the vinyl protons at C-6 and C-7 in **3f** (6.54 and 5.69) that were similar to those for **3a** (6.39 and 5.67) rather than its exo isomer **3a'** (6.30 and 5.84). Steric effects are known to slow down the Cope rearrangement of divinylcyclopropanes,[16c] and the isolation of **4** is supporting evidence that the annulation proceeds by a two-step sequence rather than by a concerted process.



(3)

When these reactions were extended to acyclic dienes (Table II), complications arose because the initial cyclopropanations were not as highly stereoselective as they were with cyclopentadiene. Rhodium(II) acetate catalyzed decomposition of **2a** in the presence of 4-methyl-1,3-pentadiene resulted in the formation of a 4:1 mixture of the cycloheptadiene **5a** and the divinylcyclopropane **6a** (Scheme I). The trans stereochemical assignment for **6a** was based on an NOE difference analysis, in which proton enhancements between the vinyl groups was absent.[21] It would appear that excellent regiochemistry favoring cyclopropanation at the more accessible double bond occurred but the stereocontrol was less effective, leading to a mixture of *cis*- and *trans*-divinylcyclopropanes. The *cis*-divinylcyclopropane **7a** cleanly rearranged to the cycloheptadiene **5a** under the reaction conditions, but the

Scheme II



trans isomer **6a** was stable and could be isolated. Previous results on the reaction of vinylcarbenoids with simple alkenes have shown that the vinyldiazomethane **2b** is much more stereoselective than **2a** in its cyclopropanation reactions.[22] A similar trend was seen in the rhodium(II) acetate catalyzed reaction of **2b** with 4-methyl-1,3-pentadiene, which generated the cycloheptadiene **5b** in 70% yield without any evidence for the presence of the *trans*-divinylcyclopropane **6b**. A slight improvement in yield (80%) was obtained by using lower reaction temperatures (0 °C) and rhodium(II) hexanoate as catalyst.

A similar level of stereoselectivity was observed in the reaction of the vinyldiazomethane **2a** with 2,4-dimethylpentadiene, which resulted in the formation of a 4:1 mixture of the cycloheptadiene **8a** and a divinylcyclopropane, which was presumed to be the trans isomer **9a** (Scheme II). In this case, however, the divinylcyclopropane could not be isolated. On attempted distillation or chromatographic purification, a 1,5-homodienyl rearrangement to the triene **10a** occurred. During prolonged chromatography, partial equilibration of the double bond at the 3-position to the 2-position in **10a** was observed. The structure of the triene **10a** was based on distinctive chemical shifts for the vinyl protons and long range COSY spectral data, in which the expected allylic coupling was clearly evident. 1,5-Homodienyl rearrangements of vinylcyclopropanes are well-precedented, but vigorous reaction conditions are usually required.[12,23] When the reaction was repeated with the vinyldiazomethane **2b**, the transformation was once again highly stereoselective, leading to the clean formation of the cycloheptadiene **8b**. The same trends were observed for the reaction of **2a** and **2b** with 2,3-dimethylbutadiene (eq 4). With **2a**, a 4:1 mixture of the cycloheptadiene **11a** and the triene **12a** was obtained, but with **2b**, only the cycloheptadiene **11b** was formed.

In order to determine the potential of this chemistry for the stereoselective synthesis of seven-membered carbocycles, the reaction of the vinylcarbenoids with dienes of defined geometry was then examined (eq 5). The vinyldiazomethane **2b** was used as the carbenoid precursor to ensure that highly stereoselective cyclopropanations would occur. The reaction of **2b** with (*E*)-1,3-pentadiene proceeded with excellent stereocontrol to produce exclusively the cis product **13a**. A similar reaction using (*Z*)-1,3-pentadiene formed the trans isomer **13b**. The stereochemical assignments of **13a** and **13b** were based on NOE analysis.[21] Most distinctive was the large enhancement of the exocyclic vinyl protons which occurred on irradiation

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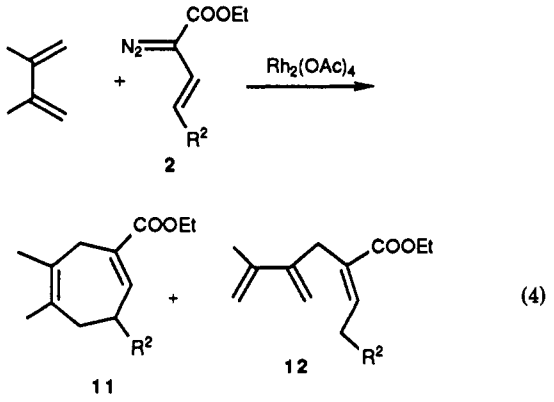
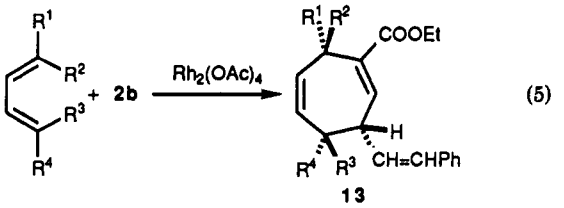


(4)

a R^2 = COOEt
b R^2 = CH=CHPh

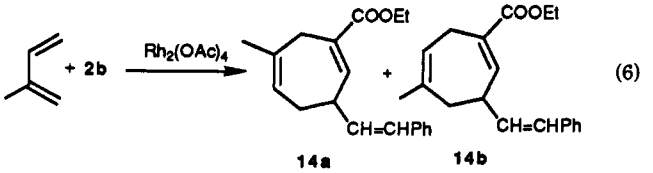
of the proton at C-4 when these two groups were on the same side of the ring. Extension of these studies to 2,4-hexadienes was only partially successful. Attempts at trapping the vinylcarbenoid derived from **2b** with (*E*,*E*)-2,4-hexadiene failed. The NMR spectrum of the crude reaction mixture, which consisted of broad signals indicative of a polymeric material, was identical with that which was obtained from decomposition of **2b** in the absence of a diene trap. On the other hand, the reaction with (*Z*,*E*)-2,4-hexadiene was quite effective, leading to **13c** with control of relative stereochemistry at three stereogenic centers. Once again, the stereochemistry of **13c** was readily assigned by NOE analysis.[21] Only a small enhancement of the exocyclic vinyl protons was observed on irradiation of the C-4 proton, while irradiation of the C-4 methyl group resulted in a significant enhancement of the C-7 proton and the exocyclic vinyl protons.



(5)

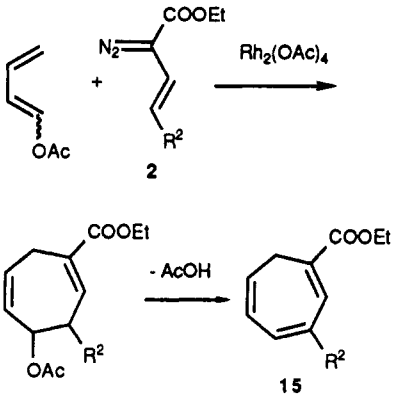
	R^1	R^2	R^3	R^4
13a	H	H	H	CH_3
13b	H	H	CH_3	H
13c	H	CH_3	H	CH_3

Unlike the reaction with terminally substituted dienes, only moderate regioselectivity was observed on decomposition of **2b** in the presence of isoprene (eq 6). A mixture of cycloheptadienes **14a** and **14b** (6:1) was obtained, which presumably arose through only moderate discrimination between the double bonds of isoprene during the cyclopropanation step. The absence of any triene products demonstrated once again the high stereoselectivity of cyclopropanation with **2b**.



(6)

The tandem cyclopropanation/Cope rearrangement sequence is also applicable for the synthesis of cycloheptatriene derivatives by using dienes with a potential leaving group. Rhodium(II) acetate catalyzed decomposition of **2a** in the presence of 1-acetoxybutadiene (*E*,*Z* mixture) resulted in an uncharacterized mixture, which on attempted purification by Kugelrohr distillation underwent elimination of acetic acid to form the cycloheptatriene **15a** (eq 7). In a similar manner, DBU treatment of the crude product from the reaction of **2c** with 1-acetoxybutadiene (*E*,*Z* mixture) resulted in the formation of **15c**.



(7)

a R_2 = COOEt
c R_2 = SO_2Ph

Discussion

As previously described by Doyle and co-workers,[24] cyclopropanations with the carbenoid from ethyl diazoacetate on 1-substituted dienes preferentially occur at the least substituted double bond, while electronic factors control the position of attack for 2-substituted dienes. The same trends were observed in this study with vinylcarbenoids, although the steric effect of functionality at the diene terminus was more pronounced. Reaction of the vinylcarbenoid from **2b** with either (*Z*)- or (*E*)-1,3-pentadiene resulted in cyclopropanation exclusively at the less substituted double bond as determined by NMR analysis. Although *Z* disubstituted double bonds were capable of trapping the vinylcarbenoid, *E* disubstituted double bonds were totally ineffective. This characteristic was clearly seen in the reaction with (*E*,*E*)-2,4-hexadiene, which failed to trap the vinylcarbenoid intermediate, and also with (*E*,*Z*)-2,4-hexadiene, where the only product, **13c**, was derived from initial cyclopropanation at the *Z* double bond.

The most startling feature of cyclopropanations with vinylcarbenoids is the remarkable level of stereoselectivity that is possible. With planar systems such as cyclopentadiene, furans,[10a,b] and pyrroles,[10c] the cyclopropanation was essentially stereospecific, although some loss in stereoselectivity was observed in this study with acyclic dienes as evidenced in the reactions of **2a**. These results should be contrasted with cyclopropanations by carbenoids derived from alkyl diazoacetates which gave rather low stereoselectivity in favor of the trans (anti) isomer (1:1.2 to 1:4)[8] unless extremely bulky derivatives were used.[9d] Low stereoselectivity (1:1.7) was also observed in the reaction of Fisher vinylcarbenoids with dienes.[11] The generally accepted model for metal-catalyzed cyclopropanation was developed by Doyle,[8b,9d,25] based primarily on his results on the stereoselectivity of cyclopropanations with alkyl diazoacetates. Essentially, the cyclopropanation was considered to proceed in a nonsynchronous manner.

(24) Doyle, M. P.; Dorow, R. L.; Tamblyn, W. H.; Buhro, W. E. *Tetrahedron Lett.* **1982**, *23*, 2261.
(25) Doyle, M. P.; Griffin, J. H.; Bagheri, V.; Dorow, R. L. *Organometallics* **1984**, *3*, 53.

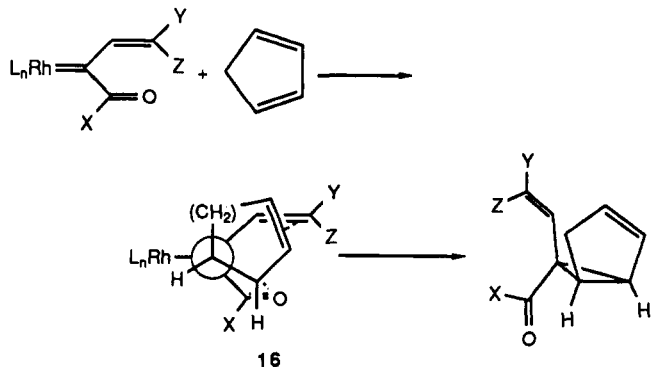


Figure 1.

Stabilization of the somewhat dipolar transition state would be achieved by interaction of the carbenoid carbonyl with the alkene. The arrangement in which the ester functionality and the alkene substituent are opposite to each other would lead to the preferential formation of the trans (anti) isomer.

Cyclopropanations with vinylcarbenoids may be rationalized according to a similar mechanism as illustrated in Figures 1 and 2, but other interactions would be required to explain the remarkable stereoselectivities observed in these reactions. The significance of carbonyl interaction in the developing transition state of vinylcarbenoid cyclopropanations is clearly evident, because in contrast to our studies, Salomon has shown that cyclopropanations with the parent vinyldiazomethane were not particularly stereoselective.[15f] If carbonyl interaction was the only factor involved, however, cyclopropanations with vinyldiazomethanes **2** would be expected to be less stereoselective than with diazoacetates, because the vinyl group would crowd the favored transition state. Assuming that the Doyle mechanism is operative in these reactions, the high stereoselectivity would require further stabilization of the transition state leading to the *cis*-divinylcyclopropanes. This could occur through interaction between the vinyl group of the carbenoid and the other double bond of the diene. This interaction would be very favorable in planar dienes (see transition state **16**), such as cyclopentadiene, furans, and pyrroles, and so far, no evidence of *trans*-divinylcyclopropanes has been observed by us in vinylcarbenoid cyclopropanations of these dienes. Cyclopropanations of acyclic dienes, however, were less stereoselective. Presumably, the π-stacking is not as favored as in the case of planar dienes, particularly as the diene would preferentially exist in an s-trans conformation (see transition state **17** vs **18**). The structure of the vinylcarbenoid has a significant effect because cyclopropanations with **2b** were far more stereoselective than with **2a**. Further confirmation that factors other than simple steric effects were involved was obtained from the reaction with isoprene. In this case, R_3 (methyl) would be the bulky group, yet the *cis*-divinylcyclopropane still predominated.

The vinylcarbenoids would be expected to be more electrophilic than the carbenoid from alkyl diazoacetate, and this may also be an important factor. The extent of dipolar character in the transition state might be anticipated to be greater, which would increase the interaction between the carbenoid carbonyl and the alkene. Indeed, we have found that reactions of vinylcarbenoids with oxygenated dienes result in exclusive formation of *cis*-divinylcyclopropanes.[26] Similarly, the stereoselectivity in vinylcarbenoid cyclopropanation of *n*-butyl vinyl ether or vinyl acetate is much higher than with allylbenzene or vinylcyclohexane.[22] Furthermore, O'Dannon and Dailey[9g] have observed enhanced stereoselectivity in cyclopropanations with ethyl nitrodiazoacetate, which would also be expected to proceed via a very electrophilic carbenoid intermediate.

The stereocontrol observed in the final products is easily understood through the involvement of *cis*-divinylcyclopropane intermediates as illustrated in Figure 2. It is well-known that the Cope rearrangement of divinylcyclopropanes proceeds through a boat transition state in which the vinyl groups point toward the cyclopropane.[12] As shown for structure **19**, the Cope rearrangement would lead to the stereochemistry observed in this study.

Even though a slight drop in cyclopropanation stereoselectivity was observed in the reaction of **2a** with acyclic dienes in comparison to our earlier studies with planar cyclic dienes, by appropriate choice of vinylcarbenoid and diene, the tandem cyclopropanation/Cope rearrangement sequence offers an effective and highly stereoselective approach to 1,4-cycloheptadienes. Due to the presence of electron-withdrawing groups, the vinyldiazomethanes used in this study have reasonable stability and are very effective vinylcarbenoid precursors.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded at 200 and 50.3 MHz, respectively. Mass spectral determinations were carried out at 70 eV. CH_2Cl_2 was freshly distilled from CaH_2. Column chromatography was carried out on silica gel 60 (230–400 mesh).

Diethyl (*E*)- and (*Z*)-2-Ethoxypent-2-enedioates (1f).[10d] A solution of **2a** (2.11 g, 9.94 mmol) in CH_2Cl_2 (10 mL) was added over 10 min to a stirred mixture of rhodium(II) acetate (0.025 g, 0.057 mmol) and ethanol (2.30 g, 50 mmol) in CH_2Cl_2 (20 mL), heated at reflux under Ar. After heating for a further 12 h, the solvent was evaporated under reduced pressure. The residue was then purified by chromatography on silica gel with ether/petroleum ether (10:90) as solvent to give **1f** as a gum, which was a 1:4 mixture of *E* and *Z* isomers: 1.89 g (83%); IR (neat) 1735, 1720, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) *Z* isomer δ 6.37 (t, 1 H, J = 7.4 Hz), 4.22 (q, 2 H, J = 7.2 Hz), 4.15 (q, 2 H, J = 7.2 Hz), 3.89 (q, 2 H, J = 7.2 Hz), 3.27 (d, 1 H, J = 7.4 Hz), 1.31 (t, 3 H, J = 7.2 Hz), 1.28 (t, 3 H, J = 7.2 Hz), 1.27 (t, 3 H, J = 7.2 Hz); *E* isomer δ 5.38 (t, 1 H, J = 7.1 Hz), 4.32 (2 q, superimposed, 4 H), 3.81 (q, 2 H, J = 7.1 Hz), 3.52 (d, 2 H, J = 7.1 Hz), 1.28 (3 t, superimposed, 9 H). Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.41; H. 7.89.

Ethyl (*E*)-2-Diazo-6-phenyl-1-hexa-3,5-dienoate (2b). DBU (2.39 g, 15.7 mmol) was added to a stirred solution of ethyl 6-phenyl-1-hexa-3,5-dienoate[27] (3.09 g, 14.3 mmol) and *p*-acetamidobenzenesulfonyl azide (3.51 g, 14.6 mmol) in acetonitrile (75 mL) at 0 °C. After the mixture was stirred for 4 h, saturated NH_4Cl solution was added, and the mixture was extracted twice with CH_2Cl_2. The organic layer was then dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. The residue was triturated with ether/pentane (50:50) and filtered, and the solvent was evaporated under reduced pressure. Further purification of the product by chromatography on silica gel with ether/pentane (20:80) as solvent gave **2b** as a red solid (mp 38–40 °C): 1.94 g (56%); IR (neat) 2100, 1710, 1635, 1605, 1460 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.20 (m, 5 H), 6.88 (ddd, 1 H, J = 15.3, 7.8, 2.4 Hz), 6.46 (d, 1 H, J = 15.3 Hz), 6.17–6.00 (m, 2 H), 4.30 (q, 2 H, J = 7.1 Hz), 1.32 (t, 3 H, J = 7.1 Hz). The vinyldiazomethanes were of insufficient stability for elemental analysis.

Ethyl (*E*)-2-Diazo-4-(phenylsulfonyl)-3-butenoate (2c). Triethylamine (2.32 g, 22.9 mmol) was added to a stirred solution of ethyl 4-(phenylsulfonyl)-3-butenoate[28] (2.55 g, 10.0 mmol) and

(26) Cantrell, W. R.; Davies, H. M. L. *J. Org. Chem.* **1991**, *56*, 723.

(27) Prepared by a Horner–Emmons reaction between phenylacetaldehyde and ethyl 4-(diethoxyphosphinyl)but-2-enoate.

(28) Prepared by hydrogen peroxide oxidation of ethyl 4-(phenylthio)-3-butenoate in acetic acid/acetic anhydride. Annunziata, R.; Barbarella, G. *Org. Magn. Reson.* **1984**, *22*, 251.

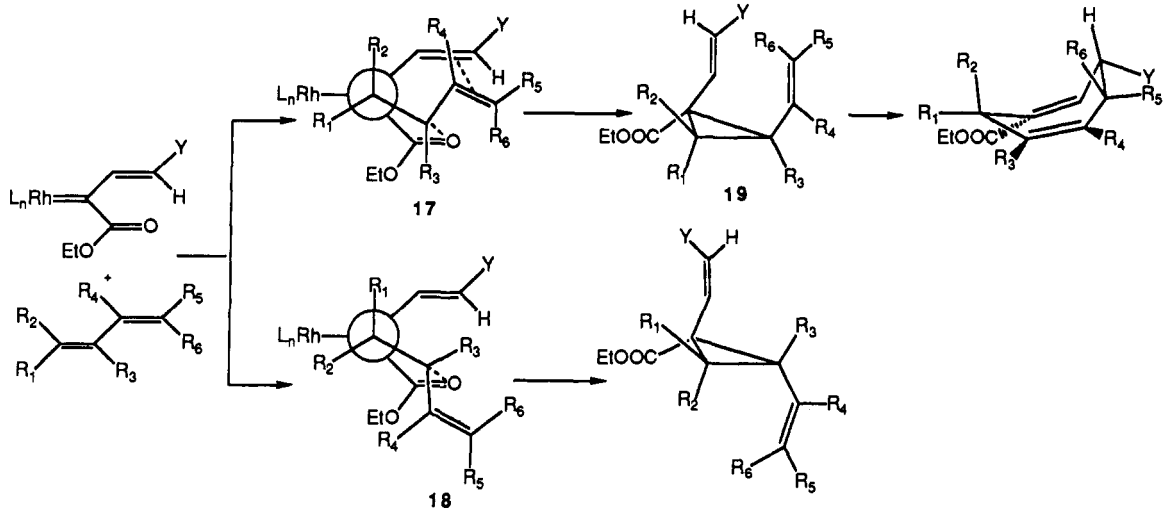


Figure 2.

p-acetamidobenzenesulfonyl azide (14.00 g, 58.3 mmol) in acetonitrile (100 mL) at 0 °C. After the mixture was stirred for 12 h, the solvent was evaporated under reduced pressure. The residue was triturated with ether/petroleum ether (50:50) and filtered, and the solvent was evaporated under reduced pressure. Further purification of the product by chromatography on silica gel with ether/petroleum ether (50:50) as solvent gave **2c** as a gum: 0.67 g (24%); IR (neat) 2120, 1700, 1600, 1450 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.00–7.85 (m, 2 H), 7.60–7.47 (m, 3 H), 7.32 (d, 1 H, J = 15.0 Hz), 6.45 (d, 1 H, J = 15.0 Hz), 4.30 (q, 2 H, J = 7.0 Hz), 1.30 (t, 3 H, J = 7.0 Hz). A small quantity of the regioisomer **ethyl 4-diazo-4-(phenylsulfonyl)-2-butenoate** was isolated: 0.04 g, (1.3%); IR (neat) 3060, 2980, 2920, 2090, 1695, 1600, 1445 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.87–7.82 (m, 2 H), 7.63–7.49 (m, 3 H), 7.08 (d, 1 H, J = 15.7 Hz), 5.66 (d, 1 H, J = 15.7 Hz), 4.15 (q, 2 H, J = 7.1 Hz), 1.23 (t, 3 H, J = 7.1 Hz).

Methyl (*E*)-2-Diazo-4-phenylbutenoate (2d). In a similar manner to the preparation of **2b**, methyl 4-phenylbutenoate[29] (2.05 g, 11.6 mmol) was converted to **2d**: 2.08 g (89%); column eluant, ether/petroleum ether (1:4); IR (neat) 3010, 2940, 2040, 1695, 1620, 1590, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34–7.15 (m, 5 H), 6.44 (d, 1 H, J = 16.2 Hz), 6.15 (d, 1 H, J = 16.2 Hz), 3.81 (s, 3 H).

3-Diazo-5-phenyl-4-penten-2-one (2e). In a similar manner to the preparation of **2b**, 5-phenyl-4-penten-2-one (3.11 g, 19.4 mmol) was converted to **2e**: 2.39 g (66%), mp 79–84 °C; column eluant, ether/petroleum ether (3:10); IR (neat) 2095, 1650, 1630, 1460 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.21 (m, 5 H), 6.56 (d, 1 H, J = 16.4 Hz), 6.19 (d, 1 H, J = 16.4 Hz), 2.33 (s, 3 H).

Diethyl (*E*)-2-Ethoxy-4-diazopent-2-enedioate (2f).[10d] In a similar manner to the preparation of **2b**, **1f** (0.63 g, 2.74 mmol) was converted to **2f**: 0.60 g (85%); column eluant, ether/petroleum ether (1:1); IR (neat) 2100, 1720, 1705, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.54 (s, 1 H), 4.28 (q, 2 H, J = 7.1 Hz), 4.19 (q, 2 H, J = 7.1 Hz), 3.92 (q, 2 H, J = 7.1 Hz), 1.33 (t, 3 H, J = 7.1 Hz), 1.30 (t, 3 H, J = 7.1 Hz), 1.25 (t, 3 H, J = 7.1 Hz).

Rhodium(II) Acetate (or Hexanoate) Catalyzed Decomposition of Vinyldiazomethanes 2 in the Presence of Alkenes. General Procedure. A solution of **2** (1 equiv) in CH_2Cl_2 (10 mL) was added over 10 min to a stirred mixture of rhodium(II) acetate (0.01–0.05 equiv) and diene in CH_2Cl_2 (10–30 mL), heated at reflux under Ar. After heating for a further 10 min, the solvent was evaporated under reduced pressure. Alternatively, a solution of **2** (1 equiv) in CH_2Cl_2 (10 mL) was added over 30 min to a stirred mixture of rhodium(II) hexanoate (0.01 equiv) and diene in CH_2Cl_2 (10–30 mL) at 10 °C in an argon atmosphere. After stirring for a further 30 min at 10 °C, the mixture was heated under reflux for 10 min. The solvent was evaporated under reduced pressure. The amounts of diazo compound (**2a–f**), rhodium(II) catalyst, and diene (see Tables I and II) used are presented in that order in abbreviated format. All products except **3a** and **15a** were purified by column chromatography on silica using ether/pentane (or ether/petroleum ether) as eluant in the ratio specified.

Diethyl *endo*-bicyclo[3.2.1]octa-2,6-diene-2,4-dicarboxylate (3a):[10d] **2a** (1.06 g, 5 mmol), acetate (0.021 g, 0.048 mmol), diene (8 mL, 97 mmol). Kugelrohr distillation gave **3a** as a gum: 1.22 g (98%); bp 130–150 °C, 0.6 mmHg; IR (neat) 1725, 1710, 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.61 (m, 1 H), 6.39 (dd, 1 H, J = 5.8, 2.9 Hz), 5.67 (dd, 1 H, J = 5.8, 2.8 Hz), 4.30–4.10 (m, 4 H), 3.45 (dd, 1 H, J = 4.6, 2.8 Hz), 3.25 (m, 2 H), 2.21 (ddd, 1 H, J = 9.8, 4.8, 4.8 Hz), 1.79 (d, 1 H, J = 9.8 Hz), 1.28 (t, 3 H, J = 7.1 Hz), 1.23 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 170.8, 165.9, 142.8, 139.4, 133.0, 130.0, 60.8, 60.6, 43.8, 42.2, 41.2, 38.0, 14.3, 14.3; MS, m/z (relative intensity) 250 (11), 209 (100), 192 (33), 163 (35), 135 (48), 119 (35), 103 (35), 91 (60); HRMS calcd for $C_{14}H_{18}O_4$ 250.1205; found 250.1200. On attempted purification by chromatography, partial isomerization of **3a** to the exo isomer **3a'** occurred: ^1H NMR ($CDCl_3$) δ 6.55 (m, 1 H), 6.30 (dd, 1 H, J = 5.6, 2.9 Hz), 5.84 (dd, 1 H, J = 5.6, 2.9 Hz), 4.30–4.10 (m, 4 H), 3.45 (m, 1 H), 3.02 (m, 1 H), 2.95 (dd, 1 H, J = 3.9, 1.3 Hz), 2.00 (ddd, 1 H, J = 9.8, 4.6, 4.6 Hz), 1.75 (d, 1 H, J = 9.8 Hz), 1.28 (t, 3 H, J = 7.1 Hz), 1.25 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 171.9, 165.7, 141.2, 139.4, 132.3, 131.1, 61.2, 60.6, 43.7, 39.7, 38.3, 38.1, 14.3, 14.3.

Ethyl *endo*-4-((*E*)-2-phenylethenyl)bicyclo[3.2.1]octa-2,6-diene-2-carboxylate (3b): **2b** (0.195 g, 0.81 mmol), acetate (0.016 g, 0.036 mmol), diene (7 mL, 85 mmol), 1:19 to 1:9 gradient; yield, 0.16 g (72%) of a gum; IR (neat) 1705, 1630, 1455 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.37–7.17 (m, 5 H), 6.47 (ddd, 1 H, J = 2.8, 1.4, 1.4 Hz), 6.45 (d, 1 H, J = 15.8 Hz), 6.40 (dd, 1 H, J = 5.7, 2.9 Hz), 6.08 (dd, 1 H, J = 15.8, 8.2 Hz), 5.71 (dd, 1 H, J = 5.7, 2.6 Hz), 4.20 (q, 2 H, J = 7.2 Hz), 3.31 (m, 2 H), 2.96 (m, 1 H), 2.23 (ddd, 1 H, J = 9.8, 4.6, 4.6 Hz), 1.85 (d, 1 H, J = 9.8 Hz), 1.30 (t, 1 H, J = 7.2 Hz); MS, m/z (relative intensity) 280 (25), 234 (18), 207 (33), 160 (22), 129 (23), 128 (23), 115 (28), 91 (100); HRMS calcd for $C_{19}H_{20}O_2$ 280.1458; found 280.1452.

Ethyl *exo*-4-(phenylsulfonyl)bicyclo[3.2.1]octa-2,6-diene-2-carboxylate (3c'): **2c** (0.15 g, 0.59 mmol), acetate (0.011 g, 0.025 mmol), diene (7 mL, 85 mmol), 1:1. Equilibration of **3c** occurred to give predominately the exo isomer **3c'**: yield, 0.15 g (80%); IR (neat) 1700, 1620, 1580, 1445 cm^{-1}; ^1H NMR ($CDCl_3$) exo isomer δ **3c'** 7.92–7.88 (m, 2 H), 7.69–7.54 (m, 3 H), 6.50 (m, 1 H), 6.33 (dd, 1 H, J = 5.7, 2.6 Hz), 5.81 (dd, 1 H, J = 5.7, 2.6 Hz), 4.23 (q, 2 H, J = 7.1 Hz), 3.53 (d, 1 H, J = 4.0 Hz), 3.43 (m, 1 H), 3.18 (m, 1 H), 1.80 (dd, 1 H, J = 10.5, 4.7, 4.7 Hz), 1.55 (d, 1 H, J = 10.5 Hz), 1.29 (t, 1 H, J = 7.1 Hz). Anal. Calcd for $C_{17}H_{18}O_4S$: C, 64.13; H, 5.70. Found: C, 64.23; H, 5.74.

Methyl *endo*-4-phenylbicyclo[3.2.1]octa-2,6-diene-2-carboxylate (3d): **1d** (2.02 g, 10 mmol), acetate (0.04 g, 0.09 mmol), diene (4.41 g, 67 mmol), 1:9; yield, 1.75 g (73%) of a gum; IR (neat) 3030, 3010, 2970, 2920, 1705, 1620, 1600, 1490, 1430 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.42–7.05 (m, 5 H), 6.65 (ddd, 1 H, J = 2.6, 1.6, 1.3 Hz), 6.37 (dd, 1 H, J = 5.6, 2.9 Hz), 5.28 (dd, 1 H, J = 5.6, 2.7 Hz), 3.80 (dd, 1 H, J = 4.4, 2.6 Hz), 3.77 (s, 3 H), 3.33 (ddd,

(29) Gerkin, R. M.; Rickborn, B. *J. Am. Chem. Soc.* **1967**, *89*, 5856.

1 H, J = 4.9, 2.7, 1.3 Hz), 3.05 (dddd, 1 H, J = 4.9, 4.4, 2.9, 1.6 Hz), 2.24 (ddd, 1 H, J = 10.0, 4.9, 4.9 Hz), 2.00 (d, 1 H, J = 10.0 Hz); MS, m/z (relative intensity) 240 (95), 225 (10), 208 (45), 181 (100), 179 (55), 165 (70), 91 (35), 77 (40); HRMS calcd for $C_{16}H_{16}O_2$ 240.1150, found 240.1147.

***endo*-2-Acetyl-4-phenylbicyclo[3.2.1]octa-2,6-diene (3e)**: **1e** (0.15 g, 0.81 mmol), acetate (0.016 g, 0.036 mmol), diene (5 mL, 61 mmol), 1:9; yield, 0.12 g (66%) of a gum; IR (neat) 1670, 1630, 1460, 1435 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.42–7.24 (m, 3 H), 7.11–7.06 (m, 2 H), 6.54 (ddd, 1 H, J = 2.5, 1.5, 1.5 Hz), 6.30 (dd, 1 H, J = 5.6, 2.8 Hz), 5.28 (dd, 1 H, J = 5.6, 2.8 Hz), 3.85 (m, 1 H), 3.49 (m, 1 H), 3.04 (m, 1 H), 2.30 (s, 3 H), 2.26 (ddd, 1 H, J = 9.9, 4.8, 4.8 Hz), 1.90 (d, 1 H, J = 9.9 Hz); MS, m/z (relative intensity) 224 (100), 181 (81), 166 (68), 165 (68), 115 (64), 91 (48), 77 (53); HRMS calcd for $C_{16}H_{16}O$ 224.1202, found 224.1200.

Ethyl 6-[(*Z*)-2-ethoxy-2-(ethoxycarbonyl)ethenyl]bicyclo[3.1.0]hex-2-ene-6-carboxylate (4):[10d] **2f** (0.53 g, 2.07 mmol), acetate (0.022 g, 0.05 mmol), diene (8 mL, 97 mmol), 1:9; yield, 0.47 g (77%) of a gum; IR (neat) 1720, 1710, 1640, 1540 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.83 (s, 1 H), 5.73–5.63 (m, 2 H), 4.19 (q, 2 H, J = 7.1 Hz), 4.11 (q, 2 H, J = 7.1 Hz), 3.93–3.82 (m, 2 H), 2.68–2.55 (m, 3 H), 2.15 (br d, 1 H, J = 16.3 Hz), 1.29 (t, 3 H, J = 7.1 Hz), 1.24 (t, 3 H, J = 7.1 Hz), 1.23 (t, 3 H, J = 7.1 Hz). Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.28; H, 7.53. Found: C, 65.36; H, 7.53.

Diethyl *endo*-4-Ethoxybicyclo[3.2.1]octa-2,6-diene-2,4-dicarboxylate (3f).[10d] A solution of **4** (0.43 g) in toluene was heated under reflux for 12 h. The solvent was then evaporated under reduced pressure, and the residue was chromatographed on silica with ether/petroleum ether (1:1) as solvent to give **3f** as a gum: 0.41 g (95%); IR (neat) 1735, 1710, 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.70 (m, 1 H), 6.54 (dd, 1 H, J = 5.6, 2.9 Hz), 5.69 (dd, 1 H, J = 5.4, 2.9 Hz), 4.29–4.13 (m, 4 H), 3.70–3.42 (m, 2 H), 3.38 (m, 1 H), 3.08 (m, 1 H), 2.18–2.03 (m, 2 H), 1.29 (t, 3 H, J = 7.0 Hz), 1.28 (t, 3 H, J = 7.0 Hz); 1.19 (t, 3 H, J = 7.0 Hz). Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.28; H, 7.53. Found: C, 65.24; H, 7.58.

Diethyl 4,4-dimethylcyclohepta-1,5-diene-1,3-dicarboxylate (5a) and ethyl 1β-[(*E*)-2-(ethoxycarbonyl)ethenyl]-2α-(2-methyl-1-propenyl)cyclopropane-1α-carboxylate (6a): **2a** (0.212 g, 1 mmol), acetate (0.0044 g, 0.01 mmol), diene (0.41 g, 5.0 mmol), 3:97; yield, 0.153 g (58%) of **5a** as a gum; IR (neat) 2980, 2960, 2900, 2880, 1700, 1650, 1460 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.09 (dd, 1 H, J = 6.9, 2.4 Hz), 5.44 (ddd, 1 H, J = 12.0, 7.6, 2.9 Hz), 5.24 (dd, 1 H, J = 12.0, 2.4 Hz), 4.16 (q, 4 H, J = 7.2 Hz), 3.73 (d, 1 H, J = 6.9 Hz), 3.20 (dd, 1 H, J = 19.3, 7.6 Hz), 3.00 (br d, 1 H, J = 19.3 Hz), 1.26 (t, 6 H, J = 7.2 Hz), 1.06 (s, 3 H), 1.05 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 172.0, 166.0, 140.1, 139.7, 134.8, 121.8, 60.3, 60.1, 53.0, 36.9, 29.3, 24.7, 23.9, 13.7, 13.7; MS, m/z (relative intensity) 266 (10), 220 (100), 205 (23), 174 (40), 147 (75), 133 (17), 119 (56), 105 (27), 93 (11); HRMS calcd for $C_{15}H_{22}O_4$ 266.1518; found 266.1517.

6a: yield, 0.0369 g, (14%) as a gum; IR ($CHCl_3$) 1715, 1643 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.61 (d, 1 H, J = 15.9 Hz), 5.62 (d, 1 H, J = 15.9 Hz), 5.01 (br d, 1 H, J = 8.2 Hz), 4.19 (q, 2 H, J = 7.1 Hz), 4.18 (q, 2 H, J = 7.1 Hz), 2.10 (ddd, 1 H, J = 8.1, 8.1, 8.1 Hz), 1.94 (dd, 1 H, J = 8.1, 4.9 Hz), 1.69 (s, 3 H), 1.67 (s, 3 H), 1.57 (dd, 1 H, unresolved), 1.28 (t, 3 H, J = 7.1 Hz), 1.25 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 169.7, 166.7, 148.2, 137.9, 120.2, 116.3, 61.0, 60.3, 36.7, 33.6, 25.5, 23.5, 18.4, 14.3, 14.2; MS, m/z (relative intensity) 266 (3), 220 (100), 205 (10), 193 (21), 174 (40), 147 (95), 133 (20), 119 (47), 103 (23), 91 (25); HRMS calcd for $C_{15}H_{22}O_4$ 266.1518, found 266.1520.

Ethyl 4,4-dimethyl-3-((*E*)-2-phenylethenyl)cyclohepta-1,5-diene-1-carboxylate (5b): **2b** (0.241 g, 1 mmol), hexanoate (0.0067 g, 0.01 mmol), diene (0.41 g, 5 mmol), 3:97; yield, 0.238 g (80%) of a gum. With rhodium(II) acetate as catalyst, **5b** was isolated in 70% yield: IR (neat) 3020, 2980, 2960, 1695, 1640, 1590, 1445 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.40–7.21 (m, 5 H), 7.01 (d, 1 H, J = 7.3 Hz), 6.47 (d, 1 H, J = 15.7 Hz), 6.27 (dd, 1 H, J = 15.7, 8.8 Hz), 5.52 (dt, 1 H, J = 12.0, 4.9 Hz), 5.36 (br d, 1 H, J = 12.0 Hz), 4.18 (q, 2 H, J = 7.0 Hz), 3.31 (dd, 1 H, J = 8.8, 7.3 Hz), 3.19 (d, 2 H, J = 4.9 Hz), 1.29 (t, 3 H, J = 7.0 Hz), 1.07 (s, 3 H), 1.04 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 167.2, 144.0, 140.2, 137.3, 132.6, 132.2, 129.2, 128.5, 127.3, 126.2, 122.8, 60.7, 52.2, 38.0, 29.9, 27.0, 26.3, 14.2; MS, m/z (relative intensity) 296 (11), 223 (22), 205 (13), 179 (10), 158 (22), 117 (18), 91 (46), 70 (46), 61 (100); HRMS calcd for $C_{20}H_{24}O_2$ 296.1772, found 296.1766.

Diethyl 4,4,6-trimethylcyclohepta-1,5-diene-1,3-dicarboxylate (8a) and ethyl 4-(ethoxycarbonyl)-6-methylene-8-methylnona-3(*E*),7-dienoate (10a): **2a** (0.212 g, 1.0 mmol), acetate (0.0044 g, 0.01 mmol), diene (0.48 g, 5.0 mmol). The residue was heated to 70 °C for 1 h to afford a mixture of **8a** and **10a** (ratio 4:1). The two components were separable by chromatography on silica with ether/pentane (3:97) as solvent to give **8a** and **10a**. **8a**: 0.177 g, 63%; IR (neat) 2975, 2925, 2860, 1715, 1700, 1650, 1470, 1450 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.10 (d, 1 H, J = 7.1 Hz), 5.05 (br s, 1 H), 4.19 (q, 2 H, J = 7.0 Hz), 4.18 (q, 2 H, J = 7.0 Hz), 3.68 (t, 1 H, J = 7.1 Hz), 3.07 (s, 2 H), 1.73 (s, 3 H), 1.29 (t, 3 H, J = 7.0 Hz), 1.28 (t, 3 H, J = 7.0 Hz), 1.05 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 172.6, 166.4, 139.9, 134.8, 133.8, 129.4, 60.6, 60.4, 53.0, 37.3, 30.1, 29.7, 27.8, 24.3, 14.1, 14.1; MS, m/z (relative intensity) 280 (7), 234 (55), 188 (85), 161 (70), 133 (90), 119 (80), 91 (72), 83 (100); HRMS calcd for $C_{16}H_{24}O_4$ 280.1674, found 280.1671.

10a: 0.0385 g, 14%; IR (CCl_4) 1731, 1710, 1652, 1516, 1465, 1446 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.03 (t, 1 H, J = 7.4 Hz), 5.56 (br s, 1 H), 4.88 (br s, 1 H), 4.76 (br s, 1 H), 4.20 (q, 2 H, J = 7.1 Hz), 4.15 (q, 2 H, J = 7.1 Hz), 3.21 (d, 2 H, J = 7.4 Hz), 3.07 (br s, 1 H), 1.74 (br s, 6 H), 1.29 (t, 3 H, J = 7.1 Hz), 1.28 (t, 3 H, J = 7.1 Hz); MS, m/z (relative intensity) 280 (12), 234 (61), 219 (13), 206 (53), 192 (80), 177 (30), 161 (60), 147 (26), 133 (100), 119 (88), 105 (36), 91 (67), 79 (51); HRMS calcd for $C_{16}H_{24}O_4$ 280.1674, found 280.1667. During prolonged chromatography, partial equilibration of the double bond at the 3-position in **10a** to the 2-position was observed.

Ethyl 4,4,6-trimethyl-3-((*E*)-2-phenylethenyl)cyclohepta-1,5-diene-1-carboxylate (8b): **2b** (0.2422 g, 1 mmol), hexanoate (0.0067 g, 0.01 mmol), diene (0.96 g, 10 mmol), 4:96; yield, 0.1842 g (59%) of a gum; IR (neat) 1730, 1680, 1495, 1480, 1415, 1400 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.39–7.21 (m, 5 H), 6.98 (dd, 1 H, J = 7.3, 1.9 Hz), 6.44 (d, 1 H, J = 15.8 Hz), 6.27 (dd, 1 H, J = 15.8, 8.9 Hz), 5.15 (br s, 1 H), 4.18 (q, 2 H, J = 7.1 Hz), 3.26 (dd, 1 H, J = 8.9, 7.3 Hz), 3.21 (br d, 1 H, J = 19.5 Hz), 3.05 (d, 1 H, J = 19.5 Hz), 1.77 (s, 3 H), 1.29 (t, 3 H, J = 7.1 Hz), 1.04 (s, 3 H), 1.01 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 167.4, 144.0, 137.4, 134.9, 132.2, 131.5, 130.1, 129.6, 128.6, 127.3, 126.2, 60.7, 51.9, 37.7, 31.6, 30.1, 27.9, 26.5, 14.3; MS, m/z (relative intensity) 310 (20), 237 (35), 181 (20), 117 (40), 105 (100), 91 (62); HRMS calcd for $C_{21}H_{26}O_2$ 310.1933, found 310.1944.

Diethyl 5,6-dimethylcyclohepta-1,5-diene-1,3-dicarboxylate (11a) and ethyl 4-(ethoxycarbonyl)-7-methyl-6-methyleneocta-3(*E*),7-dienoate (12a): **2a** (0.212 g, 1.0 mmol), acetate (0.0044 g, 0.01 mmol), diene (0.41 g, 5.0 mmol). The residue was heated to 65 °C for 1.5 h to afford a mixture of **11a** and **12a** (ratio 4:1). The two components were separable by chromatography on silica with ether/pentane (3:97) as solvent gradient to give **11a** and **12a**. **11a**: 0.131 g, 49%; IR (neat) 2980, 2900, 2880, 1725, 1700, 1640, 1450 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.96 (d, 1 H, J = 4.3 Hz), 4.18 (q, 4 H, J = 7.3 Hz), 3.40 (m, 1 H), 3.21 (d, 1 H, J = 16.3 Hz), 3.08 (d, 1 H, J = 16.3 Hz), 2.71 (dd, 1 H, unresolved, J = 13.2 Hz), 2.39 (dd, 1 H, J = 13.2, 3.4 Hz), 1.75 (s, 3 H), 1.73 (s, 3 H), 1.29 (t, 3 H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 172.8, 167.6, 137.7, 132.6, 131.0, 127.8, 61.0, 60.8, 43.3, 33.9, 31.5, 21.1, 19.9, 14.2, 14.1; MS, m/z (relative intensity) 266 (1), 220 (75), 163 (25), 147 (35), 119 (100), 105 (22), 69 (43); HRMS calcd for $C_{15}H_{22}O_4$ 266.1518, found 266.1520.

12a: 0.0332 g, 13%; FTIR ($CHCl_3$) 1721, 1654, 1466, 1446 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.08 (t, 1 H, J = 7.2 Hz), 5.10 (br s, 1 H), 5.07 (br s, 1 H), 4.97 (br s, 1 H), 4.73 (br s, 1 H), 4.15 (q, 2 H, J = 7.0 Hz), 4.12 (q, 2 H, J = 7.0 Hz), 3.24 (br s, 2 H), 3.11 (d, 2 H, J = 7.2 Hz), 1.89 (s, 3 H), 1.22 (t, 3 H, J = 7.0 Hz), 1.2 (t, 3 H, J = 7.0 Hz); MS, m/z (relative intensity) 267 (5), 266 (1), 220 (16), 206 (5), 192 (27), 179 (53), 163 (22), 147 (42), 133 (25), 119 (100), 105 (70), 91 (48), 73 (33); HRMS calcd for $C_{15}H_{22}O_4$ 266.1518, found 266.1537. During prolonged chromatography, partial equilibration of the double bond at the 3-position to the 2-position was observed.

Ethyl 5,6-dimethyl-3-((*E*)-2-phenylethenyl)cyclohepta-1,5-diene-1-carboxylate (11b): **2b** (0.2409 g, 1 mmol), hexanoate (0.0067 g, 0.01 mmol), diene (0.82 g, 10 mmol), 4:96; yield, 0.1251 g (42%) of a gum; IR (neat) 1700, 1640, 1450 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.38–7.21 (m, 5 H), 6.79 (d, 1 H, J = 4.2 Hz), 6.44 (d, 1 H, J = 16.0 Hz), 6.17 (dd, 1 H, J = 16.0, 7.7 Hz), 4.18 (q, 2 H,

J = 7.1 Hz), 3.25 (m, 1 H), 3.16 (br s, 2 H), 2.43 (m, 2 H), 1.76 (s, 3 H), 1.71 (s, 3 H), 1.29 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 168.2, 142.7, 137.3, 131.9, 131.5, 130.9, 130.3, 128.8, 128.5, 127.3, 126.2, 60.7, 41.1, 37.7, 31.6, 20.9, 20.5, 14.3; MS, m/z (relative intensity) 296 (65), 266 (25), 223 (58), 205 (35), 179 (20), 163 (22), 130 (30), 117 (60), 91 (100); HRMS calcd for $C_{20}H_{24}O_2$ 296.1776, found 296.1750.

Ethyl *cis*-4-methyl-3-((*E*)-2-phenylethenyl)cyclohepta-1,5-diene-1-carboxylate (13a): **2b** (0.2414 g, 1 mmol), hexanoate (0.0067 g, 0.01 mmol), diene (0.68 g, 10 mmol), 4:96; yield, 0.2112 g (75%) of a gum; IR (neat) 1705, 1640, 1595, 1490, 1450 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.40–7.17 (m, 5 H), 7.01 (d, 1 H, J = 6.4 Hz), 6.48 (d, 1 H, J = 15.9 Hz), 6.17 (dd, 1 H, J = 15.9, 8.1 Hz), 5.77–5.50 (m, 2 H), 4.19 (q, 2 H, J = 7.1 Hz), 3.43 (m, 1 H), 3.22 (m, 2 H), 2.78 (m, 1 H), 1.29 (t, 3 H, J = 7.1 Hz), 1.06 (d, 3 H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 167.7, 143.7, 137.3, 136.2, 131.9, 131.3, 129.2, 128.5, 127.3, 126.2, 125.9, 60.8, 46.9, 36.0, 26.6, 18.1, 14.3; MS, m/z (relative intensity) 282 (45), 154 (5), 137 (7), 209 (35), 193 (15), 167 (17), 144 (15), 131 (22), 117 (35), 91 (80), 82 (100), 55 (35); HRMS calcd for $C_{19}H_{22}O_2$ 282.1619, found 282.1624. Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 80.72; H, 7.90.

Ethyl *trans*-4-methyl-3-((*E*)-2-phenylethenyl)cyclohepta-1,5-diene-1-carboxylate (13b): **2b** (0.2414 g, 1 mmol), hexanoate (0.0067 g, 0.01 mmol), diene (0.68 g, 10 mmol), 4:96; yield, 0.1932 g (68%) of a gum; IR (neat) 1700, 1640, 1600, 1460 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.40–7.17 (m, 5 H), 6.92 (d, 1 H, J = 5.8 Hz), 6.44 (d, 1 H, J = 15.8 Hz), 6.16 (dd, 1 H, J = 15.8, 8.9 Hz), 5.72–5.49 (m, 2 H), 4.18 (q, 2 H, J = 7.1 Hz), 3.19 (m, 3 H), 2.50 (m, 1 H), 1.28 (t, 3 H, J = 7.1 Hz), 1.05 (d, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 167.5, 144.0, 137.2, 135.9, 132.6, 131.5, 131.3, 128.5, 127.3, 126.2, 126.0, 60.8, 48.1, 35.5, 26.1, 20.8, 14.3; MS, m/z (relative intensity) 282 (65), 252 (10), 209 (50), 167 (30), 129 (40), 105 (55), 91 (100), 77 (70); HRMS calcd for $C_{19}H_{22}O_2$ 282.1620, found 282.1621.

Ethyl 4α,6β-dimethyl-3α-((*E*)-2-phenylethenyl)cyclohepta-1,5-diene-1-carboxylate (13c): **2b** (0.2412 g, 1 mmol), hexanoate (0.0067 g, 0.01 mmol), diene (0.82 g, 10 mmol), 4:96; yield, 0.1556 g (53%) of a gum; IR (neat) 1700, 1640, 1598, 1490, 1450 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.40–7.18 (m, 5 H), 6.93 (d, 1 H, J = 6.3 Hz), 6.49 (d, 1 H, J = 15.9 Hz), 6.17 (dd, 1 H, J = 15.9, 8.0 Hz), 5.72–5.51 (m, 2 H), 4.19 (q, 2 H, J = 7.1 Hz), 3.54–3.42 (m, 2 H), 2.67 (m, 1 H), 1.30 (t, 3 H, J = 7.1 Hz), 1.28 (d, 3 H, J = 7.1 Hz), 1.03 (d, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 167.6, 142.8, 137.3, 135.9, 134.3, 131.6, 131.5, 130.3, 128.5, 127.3, 126.2, 60.7, 46.3, 36.6, 33.8, 20.0, 17.2, 14.3; MS, m/z (relative intensity) 296 (20), 281 (4), 167 (7), 251 (10), 223 (25), 207 (12), 192 (38), 178 (15), 165 (18), 144 (50), 119 (72), 91 (100); HRMS calcd for $C_{20}H_{24}O_2$ 296.1776, found 296.1749. Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.81; H, 8.19.

Ethyl 6-methyl-3-((*E*)-2-phenylethenyl)cyclohepta-1,5-diene-1-carboxylate (14a) and ethyl 5-methyl-3-((*E*)-2-phenylethenyl)cyclohepta-1,5-diene-1-carboxylate (14b): **2b** (0.2430 g, 1 mmol), hexanoate (0.0067 g, 0.01 mmol), diene (0.68 g, 10 mmol), 4:96; yield, 0.2047 g (72%) of a gum; IR (neat) 1705, 1640, 1450 cm^{-1}; ^{1}H NMR ($CDCl_3$) (**14a**:**14b** ratio, 6:1) **14a** δ 7.39–7.21 (m, 5 H), 6.94 (d, 1 H, J = 5.1 Hz), 6.45 (d, 1 H, J = 16.0 Hz), 6.22 (dd, 1 H, J = 16.0, 7.6 Hz), 5.50 (br t, 1 H, J = 5.9 Hz), 4.19 (q, 2 H, J = 7.1 Hz), 3.40 (m, 1 H), 3.19 (br s, 2 H), 2.33 (br t, 2 H, J = 5.5 Hz), 1.79 (s, 3 H), 1.30 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) **14a** δ 167.8, 144.2, 137.2, 132.0, 130.7, 130.3, 130.1, 128.3, 127.3, 126.2, 122.8, 60.8, 41.2, 31.4, 30.5, 26.1, 14.3. Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 80.76; H, 7.90.

Diethyl cyclohepta-1,3,5-triene-1,3-dioate (15a): **2a** (1.06 g, 5.0 mmol), acetate (0.022 g, 0.05 mmol), diene (1.10 g, 9.8 mmol). Kugelrohr distillation gave **15a** as a gum: 0.59 g (50%); bp 135–160 °C, 0.6 mmHg; IR (neat) 1715, 1620, 1540, 1450 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.86 (d, 1 H, J = 6.1 Hz), 7.74 (s, 1 H), 6.41 (dd, 1 H, J = 9.3, 6.1 Hz), 5.87 (dt, 1 H, J = 9.3, 7.0 Hz), 4.33 (q, 2 H, J = 7.1 Hz), 4.26 (q, 2 H, J = 7.1 Hz), 2.70 (d, 2 H, J = 7.0 Hz), 1.37 (t, 3 H, J = 7.1 Hz), 1.33 (t, 3 H, J = 7.1 Hz); MS, m/z (relative intensity) 236 (15), 207 (100), 191 (33), 180 (6), 179 (30), 163 (24), 135 (46), 119 (14), 105 (8), 91 (20), 77 (17); HRMS calcd for $C_{13}H_{16}O_4$ 236.1048, found 236.1050. Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 66.19; H, 6.87.

Ethyl 3-(phenylsulfonyl)cyclohepta-1,3,5-trien-1-oate (15c): **2c** (0.36 g, 1.28 mmol), acetate (0.008 g, 0.018 mmol), diene (0.58 g, 5.18 mmol). Triethylamine (0.5 mL) in ethanol (30 mL) was added to the crude product, and the mixture was heated under reflux for 1 h. The residue was purified by chromatography on silica with ether/pentane (20:80 to 50:50) as solvent gradient to give **15c** as a gum: 0.25 g (67%); IR (neat) 1710, 1655, 1635, 1450 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.91 (s, 1 H), 7.74 (m, 3 H), 7.68–7.40 (m, 4 H), 6.45 (dd, 1 H, J = 9.1, 6.1 Hz), 5.81 (dt, 1 H, J = 9.1, 7.1 Hz), 4.21 (q, 2 H, J = 7.0 Hz), 2.60 (d, 2 H, J = 7.1 Hz), 1.29 (t, 3 H, J = 7.0 Hz); MS, m/z (relative intensity) 304 (4), 275 (21), 191 (33), 258 (6), 179 (7), 162 (10), 125 (31), 119 (14), 105 (8), 88 (20), 77 (17); HRMS calcd for $C_{16}H_{16}O_4S$ 304.0769, found 304.0777.

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Supplementary Material Available: NOE data for compounds **4**, **6a**, and **13a–c**, long range COSY data for **10a**, and copies of NMR spectra of new compounds for which combustion analysis is unavailable (36 pages). Ordering information is given on any current masthead page.