1146 *J. Org. Chem.* **1992**, *57*, 1146–1150

Stereochemical Features of the (2 + 2) Cycloaddition Reactions of Chiral Allenes. 4. The Cycloaddition of Enantioenriched 1,3-Dimethylallene with Methyl Propiolate

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The cycloaddition of methyl propiolate (MP) with enantioenriched 1,3-dimethylallene (13DMA) has been investigated. Two cycloadducts, 16 and 17, are formed in which >40% of the enantiomeric excess (ee) of 13DMA has been transferred to the cycloadducts. Ab initio calculations have been carried out on models for the diradical intermediates formed in this process. A single minimum-energy conformation appears to exist in which the alkenyl radical portion of the intermediates is oriented essentially perpendicular to the plane of the allyl radical. Energy barriers have been calculated for the 180° rotation about the newly formed C–C bond in the intermediates, which would result in their racemization. These energy barriers appear to be higher than those for ring closure. Molecular modeling calculations have been carried out to determine the lowest-energy approach of the MP to the 13DMA which indicate a near-perpendicular approach of the reactants to the transition state for diradical intermediate formation directly leading to the lowest-energy conformations of the intermediates. A detailed description of the cycloaddition process is presented which indicates that the anti,syn diradical intermediate 14 is preferentially formed and undergoes predominant ring closure to the *syn*-methyl-substituted end of the allyl radical. On the basis of our prior successful molecular modeling calculations for predicting the preferred conformations for approach of the reactants to the transition states for diradical intermediate formation and the absolute configuration of the cycloadducts, the same configurations at C_4 as shown are predicted for the two cycloadducts formed in this cycloaddition reaction.

Introduction

In the previous papers in this series were described the results of studies of the stereochemical features of the two-step, diradical-intermediate formation in (2 + 2) cycloaddition reactions of enantioenriched 1,3-dimethylallene (13DMA) with the monosubstituted radicophiles acrylonitrile (ACN) and methyl acrylate (MAC),[1] the 1,1-disubstituted radicophiles 1,1-dichloro-2,2-difluoroethene (1122) and 1,1-diphenylethene (DPE),[2] and the 1,2-disubstituted radicophiles *N*-phenylmaleimide (NPMI) and dimethyl fumarate (DMFM).[3] In the cycloaddition reactions with NPMI and DMFM, a new tetrahedral stereogenic center is formed during the irreversible formation of the diradical intermediates. In both of these reactions there are three independent, minimum-energy pathways leading to the formation of discrete conformations of the diradical intermediates which close to specific cycloadducts. The three pathways of both cycloaddition reactions differ in the extent of the transfer of the enantiomeric excess (ee) of the 13DMA to the intermediates and cycloadducts. The major cycloadduct derived in the cycloaddition reaction of 13DMA with DMFM is formed with >96% transfer of the ee of the 13DMA to the diradical intermediate and cycloadduct! In the cycloaddition of 13DMA with 1122 and DPE the anti,anti diradical intermediates possess an internal plane of symmetry (and thus are racemic) while the anti,syn diradical intermediates do not possess an internal plane of symmetry and thus are chiral. No tetrahedral stereogenic center is formed in these two cycloaddition processes. The diradical intermediates formed in the cycloaddition of 13DMA with 1122 are formed irreversibly with >30% transfer of the ee of the 13DMA to the major cycloadduct. In the reaction of DPE with 13DMA, diradical intermediate formation is reversible, resulting in the racemization of the 13DMA. The diradical intermediates formed in the cycloaddition reactions of 13DMA with ACN and MAC contain a stereogenic radical center and are chiral. In the reaction of 13DMA with ACN, 37% and 29% of the ee of the starting 13DMA is transferred to the two cycloadducts, while in the reaction with MAC, 44% and 46% of the ee of the starting 13DMA is transferred to the two cycloadducts. Molecular modeling calculations on the reaction pathway for the reaction of (*R*)-(−)-13DMA with ACN resulted in the prediction that the cycloadducts should possess the *R* configuration, consistent with the earlier observations by Baldwin and Roy.[4]

Our earlier observations that 1,1-dimethylallene undergoes smooth (2 + 2) cycloaddition with the substituted alkynes methyl propiolate and phenylacetylene[5] has led us to investigate the stereochemical features of the cycloaddition of enantioenriched 13DMA with substituted alkynes. This paper reports the results of such a study on the cycloaddition of enantioenriched 13DMA with methyl propiolate (MP). (The cycloaddition reaction of 13DMA with phenylacetylene was also carried out but it was possible to determine the ee's of the cycloadducts.) The reaction of 13DMA with MP will result in the formation of the two diradical intermediates 1 and 2. Intermediate 1 is chiral, unless the intermediate prefers to exist in an all-planar structure, and will produce optically active products. Intermediate 2 is achiral and on ring closure will produce only racemic product. The following will describe the results of this study, as well as the results of ab initio and molecular modeling calculations on the approach to the transition state for formation of the diradical intermediates and on the conformational preferences and structures of the diradical intermediates.

Results

Cycloaddition of 13DMA with MP. The cycloaddition of enantioenriched 13DMA with MP was carried out in toluene-d_8 solution in a sealed NMR tube at 130 °C for 24 h. Analysis by NMR spectroscopy indicated the formation of only the two cycloadducts 3 and 4 in a ratio of 41.8:58.2, along with some remaining unreacted 13DMA in one run (see Scheme I). The tube was opened and the

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[1] Pasto, D. J.; Sugi, K. D. *J. Org. Chem.* **1991**, *56*, 3795.
[2] Pasto, D. J., Sugi, K. D. *J. Org. Chem.* **1992**, *57*, 12.
[3] Pasto, D. J.; Sugi, K. D. *J. Org. Chem.* **1991**, *56*, 6216.
[4] Baldwin, J. E.; Roy, U. V. *J. Chem. Soc. D* **1969**, 1225.
[5] Pasto, D. J.; Kong, W. *J. Org. Chem.* **1988**, *53*, 4807.

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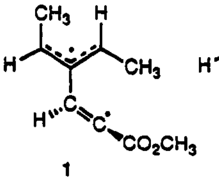
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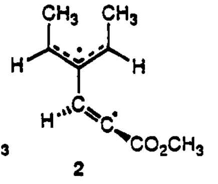
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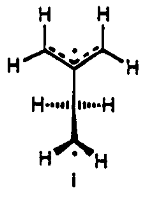
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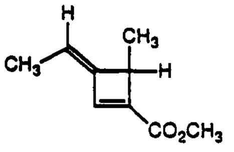
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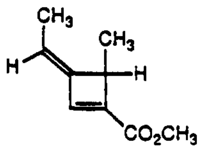
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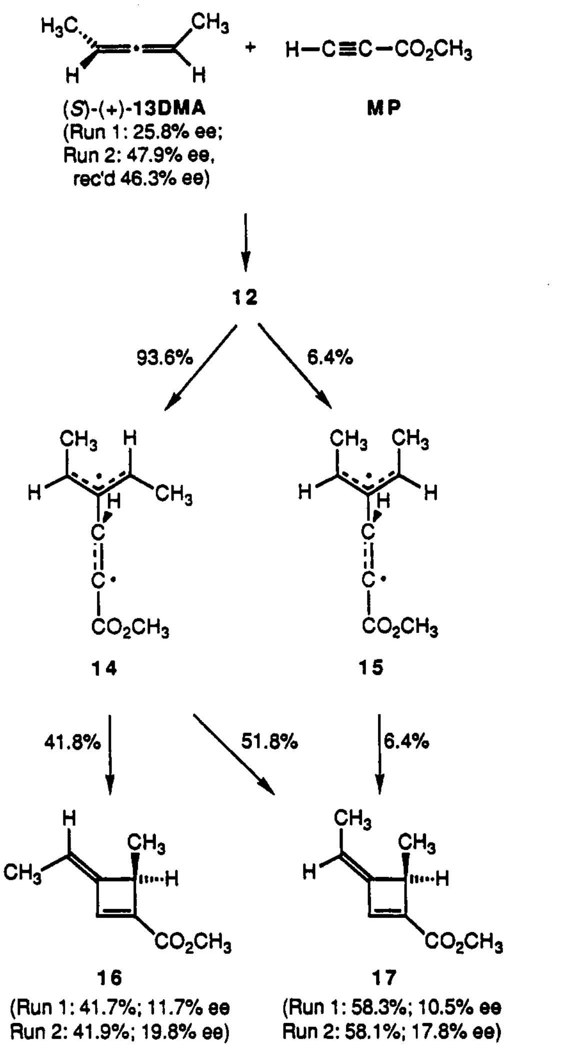
volatiles were removed on a vacuum line. The ee of the recovered 13DMA was determined directly on the volatile fraction by the use of a mixture of the NMR shift reagents Ag(fod) and chiral Yb(hfc)$_3$.[6,7] The ee's of the starting and recovered 13DMA are given in Scheme I.

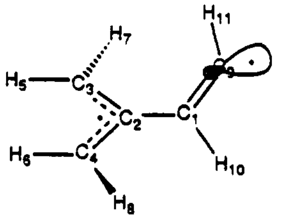
The nonvolatile residue was quickly chromatographed on silica gel, giving an inseparable mixture of **3** and **4**. The stereochemistry about the exocyclic double bond has been assigned on the basis of the results of NOE experiments. Irradiation of the vinyl proton H_3 of **3** resulted in an increase in the relative intensity of the H_2 resonance by 5.6%. Irradiation of H_2 of **3** had no effect on the relative intensity of the CH_{3b} resonance. Irradiation of H_3 of **4** has no effect on the relative intensity of H_2, while irradiation of H_2 resulted in an increase in the relative intensity of the CH_{3b} resonance of 5.0%.

The ee's of **3** and **4** have been determined directly by NMR by the use of a chiral Eu NMR chemical shift reagent. The measured ee's are given in Scheme I.

Ab Initio and Molecular Modeling Calculations. Ab initio theoretical calculations have been carried out on the configurations and conformations of the parent diradical **5–8** and on the *syn*-methyl derivatives **9–10**. Initial calculations were carried out on the triplet state[8] of the perpendicular conformations **5** and **6** at the 4-31G and 6-31G* levels using the GAUSSIAN86 program.[9] Calculation of the natural orbital populations[10] of **6** indicated significant electron population in the C_1–C_9 π^* and allyl π^* MOs, requiring higher-level calculations.[11] Subsequent CASSCF/4-31G optimization calculations on the singlet and triplet states of **5** and **6** were carried out using the GAMESS program.[12] The total energies derived from these calculations are given in Table I and the calculated structural parameters are given in Table II. Frequency calculations on the 4-31G-optimized structures of **5** and **6** indicated the presence of no imaginary frequencies.

Scheme I

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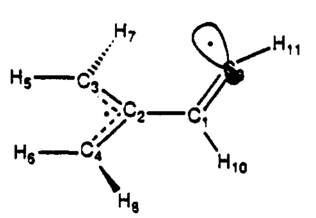
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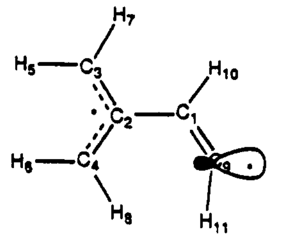
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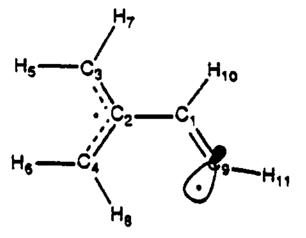
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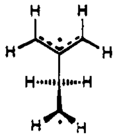
[6] Pasto, D. J.; Sugi, K. D. *J. Org. Chem.* **1991**, *56*, 4157.

[7] Mannschreck, A.; Munninger, W.; Burgemeister, T.; Gore, J.; Cazes, B. *Tetrahedron* **1986**, *42*, 399.

[8] Previous ab initio calculations on the parent homotrimethylenemethane diradical i have indicated that the triplet state lies very close in energy to the singlet (0.77 kcal mol^{-1}) and that they possess essentially identical geometries, indicating that there is no communication between the allyl and alkyl radical centers (Pasto, D. J., Benn, D. C. *J. Org. Chem.* **1991**, *56*, 6209). These results indicate that the simplier UHF triplet calculations can adequately describe the energy surface of the corresponding open-shelf singlet species.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[10] Pulay, P.; Hamilton, T. P. *J. Chem. Phys.* **1988**, *88*, 4926.

[11] The calculated natural orbital populations of **6** are MO 16 (π allyl), 1.8893; MO 17 (π C_1–C_9), 1.8501; MO 18 (π_n allyl), 1.0000; MO 19 (=C$^\bullet$), 1.0000; MO 20 (π^* C_1–C_9), 0.1499; and MO 21 (π^* allyl), 0.1107. These calculations include 20 configurations for the singlet state and 15 configurations for the triplet state.

[12] GAMESS, Dupuis, M.; Spangler, D.; Wendoloski, J. J. National Resources for Computations in Chemistry, Berkeley, CA.

Table I. Total Energies (au), $\langle S\rangle^2$ Values, and Relative Energies (kcal mol^{-1}) of 5–8[a]

basis set	5	6	7	8
4-31G(T)	−192.43075 ⟨2.5131⟩ (0.00)	−192.42996 ⟨2.5134⟩ (0.50)	−192.42697 ⟨2.3538⟩ (2.37)	−192.42848 ⟨2.3510⟩ (1.42)
CASSCF(T)	−192.46876 (0.00)	−192.46814 (0.39)		
CASSCF(S)	−192.46829 (0.00)	−192.46873 (−0.28)		
6-31G*(T)	−192.70198 ⟨2.4576⟩ (0.00)	−192.70103 ⟨2.4569⟩ (0.60)		−192.70061 ⟨2.2830⟩ (0.86)

[a] The $\langle S\rangle^2$ values are given in brackets and the relative energies are given in parentheses.

Table II. Calculated Structural Parameters for 5 and 6

	5				6			
parameter	4-31G	CASSCF(T)	CASSCF(S)	6-31G*	4-31G	CASSCF(T)	CASSCF(S)	6-31G*
				Bond Lengths				
C_1-C_2	1.501	1.499	1.501	1.503	1.500	1.498	1.496	1.502
$C_2-C_{3,4}$	1.392	1.389	1.389	1.394	1.391	1.389	1.389	1.393
C_1-C_9	1.334	1.325	1.324	1.329	1.333	1.324	1.324	1.328
$C_{3,4}-H_{5,6}$	1.073	1.072	1.072	1.075	1.073	1.072	1.072	1.075
$C_{3,4}-H_{7,8}$	1.071	1.071	1.071	1.073	1.071	1.070	1.070	1.074
C_1-H_{10}	1.076	1.076	1.077	1.079	1.080	1.079	1.079	1.082
C_9-H_{11}	1.069	1.070	1.069	1.072	1.069	1.070	1.070	1.074
				Bond Angles				
$C_1-C_2-C_{3,4}$	118.84	118.82	118.81	118.96	118.90	118.84	118.85	118.99
$C_2-C_1-C_9$	122.94	123.39	125.14	122.58	123.60	123.80	124.23	123.81
$C_2-C_{3,4}-H_{5,6}$	120.96	120.99	120.96	120.86	120.98	120.99	121.00	120.85
$C_2-C_{3,4}-H_{7,8}$	121.49	121.52	121.48	121.45	121.51	121.53	121.52	121.47
$C_2-C_1-H_{10}$	117.82	117.03	116.01	117.75	116.53	116.51	116.35	116.93
$C_1-C_9-H_{11}$	134.45	133.89	134.45	133.62	134.62	133.90	133.78	133.80

Calculations were also carried out on the C_s structures 7 and 8 at the 4-31G and 6-31G* levels; however, starting from slightly non-C_s structures resulted in the rapid approach to 5 and 6, and frequency calculations on the planar C_s structure 7 at the 4-31G level showed the presence of one imaginary frequency corresponding to rotation about the C_1-C_2 bond indicating that 7 and 8 represent transition structures for the 180° rotation about the C_1-C_2 bonds in 5 and 6.[13] The calculated structural parameters for 5 and 6 are given in Table II and for 7 and 8 in Table III.

Geometry optimization calculations have also been carried out on 9–11 at the 4-31G level in order to estimate the energy barrier for rotation about the C_1-C_2 bond in the anti,syn diradical intermediate 1 which would represent the lowest-energy pathway for racemization of 1.[14] Frequency analysis on structure 10 indicates the presence of two imaginary frequencies corresponding to rotation about both the C_1-C_2 and C_4-C_7 bonds and thus does not represent a transition structure for rotation (racemization) about the C_1-C_2 bond. Structure 11 possesses only one imaginary frequency that corresponds to rotation about the C_1-C_2 bond. The total energies of 9–11 are given in Table I and the calculated structural parameters are given in Table IV.

Molecular modeling conformational calculations have been carried out on the conformational potential energy surface for the approach of the MP to (*S*)-(+)-13DMA for diradical intermediate formation using the Chem-X program.[15] The MP and 13DMA were first geometry optimized and then "docked" such that the axes of the two 2p AOs involved in bond formation were coincident with a C–C separation of 2 Å. Then a potential energy surface scan was carried out for a 360° rotation about the $C_2-C_1-C_{1'}-C_{2'}$ dihedral angle. Two minimum-energy conformations were found, having the conformations shown in 12 and 13, with 12 being lower in energy by 1.3 kcal mol^{-1}. The $C_2-C_1-C_{1'}-C_{2'}$ dihedral angle in 12 is ~80°.

Table III. Calculated Structural Parameters for C_s 7 and 8

	7	8	
parameter	4-31G	4-31G	6-31G*
	Bond Lengths		
C_1-C_2	1.500	1.509	1.505
C_2-C_3	1.386	1.387	1.386
C_2-C_4	1.393	1.397	1.392
C_1-C_9	1.319	1.313	1.320
C_3-H_5	1.072	1.075	1.072
C_3-H_7	1.072	1.075	1.072
C_4-H_6	1.072	1.074	1.072
C_4-H_8	1.071	1.073	1.070
C_1-H_{10}	1.080	1.082	1.076
C_9-H_{11}	1.067	1.071	1.067
	Bond Angles		
$C_1-C_2-C_3$	117.99	118.02	117.53
$C_1-C_2-C_4$	120.19	120.38	120.96
$C_2-C_1-C_9$	125.19	126.19	127.06
$C_2-C_3-H_5$	121.15	121.02	121.09
$C_2-C_3-H_7$	121.76	121.71	121.71
$C_2-C_4-H_6$	120.78	120.56	120.59
$C_2-C_4-H_8$	121.72	121.71	122.34
$C_2-C_1-H_{10}$	115.30	115.61	114.88
$C_1-C_9-H_{11}$	135.21	134.31	127.38

Discussion

Theoretical Studies. One of the objectives of this study was to determine by theoretical calculations the structure(s) of the diradical intermediates formed in the (2 + 2) cycloaddition reactions of substituted allenes with alkynes and to determine if there is any appreciable interaction between the two radical centers in the minimum-energy structure(s). Two minimum-energy conformations were located for the singlet and triplet species having the perpendicular conformation and orientation of the C_9-H_{11} bond shown in structures 5 and 6. At the UHF 4-31G and 6-31G* levels the triplet state of 5 resides 0.50 and 0.60 kcal mol^{-1} lower in energy. At the CASSCF/4-31G fully geometry optimized level the triplet state of structure 5 is calculated to be lower in energy by 0.39 kcal mol^{-1}; however, similar calculations on 6 indicate that the singlet state is lower in energy by 0.28 kcal mol^{-1}. For

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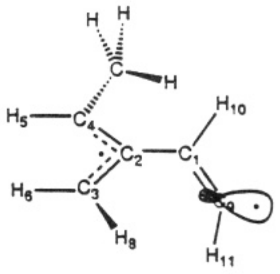
(13) In the parent homotrimethylenemethane system (i), the planar Cs structure is a true minimum-energy structure. In planar i the two hydrogens attached to the alkyl radical center are gauche to the C_3-H_8 bond, whereas in 7 or 8 the C_9-H_{11} bond or the radical center is eclipsed with the C_5-H_7 bond.

(14) Severe convergence problems were encountered in the 6-31G*-level calculations on 7 and convergence could not be accomplished.

(15) Chem-X, Distributed by Chemical Design, Ltd., Oxford, England.



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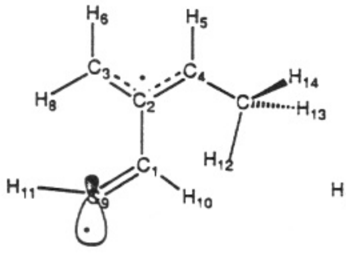

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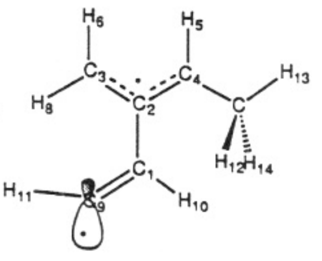

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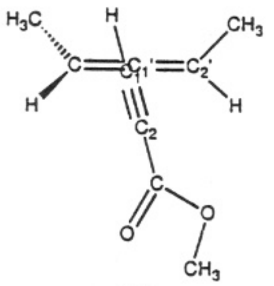

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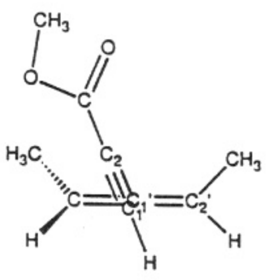

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Table IV. Calculated Structural Parameters for 9–11

parameter	9	10	11
	Bond Lengths		
C_1–C_2	1.501	1.505	1.505
C_2–C_3	1.393	1.391	1.391
C_2–C_4	1.396	1.395	1.393
C_4–C_7	1.498	1.499	1.503
C_1–C_9	1.334	1.321	1.320
C_4–H_5	1.071	1.076	1.074
C_3–H_6	1.073	1.072	1.072
C_3–H_8	1.071	1.070	1.070
C_7–H_{12}	1.080	1.078	1.082
C_7–H_{13}	1.085	1.086	1.085
C_7–H_{14}	1.087	1.086	1.085
C_1–H_{10}	1.076	1.073	1.074
C_9–H_{11}	1.069	1.067	1.067
	Bond Angles		
C_1–C_2–C_3	118.09	119.62	120.25
C_1–C_2–C_4	120.43	120.69	119.28
C_2–C_4–C_7	126.17	128.86	126.14
C_2–C_1–C_9	122.99	126.55	126.70
C_2–C_4–H_5	117.30	116.27	117.04
C_2–C_3–H_6	120.98	120.59	120.60
C_2–C_3–H_8	121.48	122.45	122.41
C_4–C_7–H_{12}	112.03	113.82	110.40
C_4–H_7–H_{13}	110.07	110.55	112.08
C_4–H_7–H_{14}	111.15	110.55	112.08
C_2–C_1–H_{10}	117.41	116.34	115.82
C_1–C_9–H_{11}	134.37	137.49	137.47
	Dihedral Angles		
C_1–C_2–C_3–C_4	180.00	180.00	180.0
C_1–C_2–C_4–C_8	0.00	0.00	0.00
C_1–C_2–C_4–H_5	180.00	180.00	180.0
C_1–C_2–C_3–H_6	180.00	180.00	180.0
C_1–C_2–C_3–H_8	0.00	0.00	
H_{12}–C_7–C_4–C_2	9.01	0.00[a]	180.0
H_{13}–C_7–C_4–C_2	129.59	121.01	60.36
H_{14}–C_7–C_4–C_2	248.25	−121.01	−60.36
C_9–C_1–C_2–C_3	82.20	0.00[a]	0.00[a]
H_{10}–C_1–C_2–C_9	180.00	180.00[a]	180.00[a]
H_{11}–C_9–C_1–C_2	0.00	0.00[a]	0.00[a]

[a] Not optimized.

structure **5** the triplet state is calculated to be lower in energy than the singlet state by 0.29 kcal mol^{-1}, while for **6** the singlet state is calculated to be lower in energy by 0.37 kcal mol^{-1}. The results of these calculations indicate that the singlet and triplet states lie very close in energy. In addition, the calculated geometries of the singlet and triplet states are virtually identical (see Table II). Overall, the results of these calculations indicate that there is no interaction between the two radical centers in such diradical intermediates and that UHF triplet calculations on more highly substituted intermediates will adequately represent the singlet state that is formed in these (2 + 2) cycloaddition processes.[8]

Starting with the all-planar C_s structure **7**, geometry optimization was accomplished. However, frequency calculations indicated that the structure possesses one imaginary frequency and thus represents the transition structure for a 180° rotation about the C_1–C_2 bond in **5**. The energy barrier for this rotation at the 4-31G level is 2.37 kcal mol^{-1}. This would represent the energy barrier for racemization of a chiral, unsymmetrically anti,anti-disubstituted diradical intermediate in which the configuration at the radical center is maintained. This energy barrier appears to be in the range of those for ring closure, and racemization might be expected to occur to some extent. The lowest-energy, all-planar structure is calculated to be **8**, which lies 0.95 kcal mol^{-1} lower in energy compared to **7**.

The UHF/4-31G calculations on the triplet state[8] for the *syn*-methyl-substituted diradical indicated the existence of a single minimum-energy conformation **9**, again having the alkenyl radical portion essentially perpendicular to the plane of the allyl radical portion of the intermediate (see Table III). The energy barrier for a 180° rotation about the C_1–C_2 bond of **9** through **11** is calculated to be ~3.7 kcal mol^{-1}. The energy barrier for a 180° rotation in the opposite direction was not calculated, but it is expected to be significantly greater in magnitude.[8]

Stereochemical Analysis of Product Formation. A mechanistic scheme for the formation of the cycloadducts **3** and **4**, including absolute stereochemistry, is illustrated in Scheme I. The approach of the MP to (*S*)-(+)-13DMA shown in **12** is favored over the approach shown in **13**. Collapse of **12** to the diradical intermediates **14** and **15** will produce the intermediates possessing the absolute configurations shown, with **15** existing in a perpendicular conformation calculated to be lowest in energy for the parent system, and **14** existing in a slightly nonperpendicular conformation as calculated for **9** (C_9–C_1–C_2–C_3 dihedral angle of 82.2°).[16] Intermediate **14** is chiral and on least-motion ring closure from the bottom face of the allyl radical will produce chiral **16** and **17**, both having the same configuration at C_4. (Structure **16** has been rotated 180° in space from its original orientation in space on ring closure of **14**.) Racemization of **14** requires a 180° rotation

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(16) Although the radical center in the parent system **9** is calculated to be nonlinear, the presence of the ester functional group in **13** and **14** may well result in a change in the geometry at the radical center. This will, however, have no effect on the arguments made concerning racemization and ring closure.

about the C_1–C_2 bond which, based on the results of the calculations on **9** and **11**, would require surmounting an energy barrier of at least ~3.7 kcal mol^{-1}. The results of our earlier studies on the stereochemical features of the (2 + 2) cycloaddition reactions of enantioenriched 13DMA with substituted alkene radicophiles[1,3] have suggested that the energy barriers for the ring closure of homotrimethylenemethane diradical intermediates are in the range of ~2–2.5 kcal mol^{-1}. The energy barriers for the ring closure of **14** and **15** are expected to be in the same range. Thus, the racemization of **14** prior to ring closure is not expected to occur to any significant degree. Intermediate **15**, however, is achiral, and can undergo ring closure to form only racemic **17**. Any reaction proceeding via approach **13** will result in the formation of cycloadducts possessing the opposite configuration of that shown in Scheme I.

The ee's of the starting 13DMA and the cycloadducts are given under the structures in Scheme I. In the first run, starting with 25.8% ee 13DMA, unreacted 13DMA could not be isolated. In the second run, starting with 47.9% ee 13DMA, unreacted 13DMA was recovered and was shown to possess 46.3% ee. This is within experimental error limits of that of the ee of the starting 13DMA and indicates that diradical intermediate formation is irreversible. Cycloadduct **16** has been formed with an average 43% transfer of the ee from the starting 13DMA, and **17** an average of 39% transfer of ee.

The facts that intermediate **15** can give rise to only racemic **17** and that **17** possesses an ee comparable with that of **16** indicate that the majority of **17** is produced from chiral **14**. If one assumes that both **16** and **17** are formed from **14** with the same extent of transfer of the ee of **14**, it is then possible to apportion the relative extent of ring closure of **14** to the anti and syn ends of the allyl radical in **14** and the relative extent of formation of the diradical intermediates **14** and **15**. The percentages are given beside the reaction arrows in Scheme I. The results indicate that there is a high preference for the formation of the anti,syn diradical intermediate **14** and, somewhat surprisingly, **14** prefers to undergo ring closure to the *syn*-methyl-substituted end of the allyl radical. *This represents the first case in which such a detailed analysis has been possible for the relative extent of the formation of the two stereoisomeric diradical intermediates in a (2 + 2) cycloaddition reaction of a substituted allene and the regioselectivity of ring closure of an anti,syn-disubstituted diradical intermediate.* Unfortunately, it is not possible to assess to what extent pathways through **12** and **13** are operative and thus to what extent the ee of the 13DMA is really transferred to the diradical intermediates.

Finally, our earlier success with use of molecular modeling calculations on the conformations for the approach of acrylonitrile to (*R*)-(−)-13DMA, which correctly predicted the absolute configuration of the diradical intermediates and cycloadducts characterized by Baldwin and Roy,[4] leads to the prediction that the least motion ring closure from the underside of the diradical intermediate **14** to form **16** and **17** will result in the formation of cycloadducts having the configuration at C_4 as shown in Scheme I.

Summary

The (2 + 2) cycloaddition of MP with enantioenriched 13DMA proceeds with >40% transfer of the ee of the 13DMA to the highly preferred chiral, anti,syn diradical intermediate **14**, which preferentially undergoes ring closure to form the *E*-cycloadduct **17**. Racemization of **14** by a 180° rotation about the C_1–C_2 bond does not appear to be competitive with ring closure.

Experimental Section

Cycloaddition of Enantioenriched (*S*)-(+)-1,3-Dimethylallene (13DMA) with Methyl Propiolate (MP). In NMR tubes were placed 14 mg (0.2 mmol) of (*S*)-(+)-13DMA (run 1; $\alpha = 0.261 \pm 0.001°$, $c = 1.250$ in diethyl ether at 25 °C, 25.8% ee; run 2, $\alpha = 0.355 \pm 0.001°$, $c = 0.915$ in diethyl ether at 25 °C, 47.9% ee),[6] 17 mg (0.2 mmol) of MP, 20 μL of toluene-d_8, and ~3 mg of hydroquinone. The contents of the tubes were triply freeze–degassed (liquid N_2) and were sealed under a vacuum. The tubes were heated in a sand bath at 130 °C for 24 h. The tubes were opened and 0.5 mL of $CDCl_3$ was added and the NMR spectra were recorded, indicating >70% disappearance of the reactants and the formation of only cycloadducts **16** and **17**. There was no evidence of any significant oligomerization or polymerization of the reactants or cycloadducts. The ratio of cycloadducts **16** and **17** was determined to be 41.9:58.1 for run 1 and 41.7:58.3 for run 2.

The volatiles from the two samples were removed on a vacuum line and were analyzed by NMR spectroscopy. Insufficient 13DMA was recovered from run 1 to determine its ee. The direct determination of the ee of the 13DMA recovered from run 2 was accomplished by the use of a 3:1 mixture of (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)silver [Ag(fod)] and chiral tris[3-[(heptafluoropropyl)hydroxymethylene]-(+)-camphorato]ytterbium(III) [$Yb(hfc)_3$] until base-line resolution of the vinyl proton or vinyl methyl resonances was achieved under double-resonance conditions. The result is given in Scheme I.

The residue was subjected to quick column chromatographic purification, giving an inseparable mixture of **16** and **17**. NMR spectrum of **16** ($CDCl_3$): δ 1.25 (d, J = 6.91 Hz, 3 H), 1.77 (d, J = 7.07 Hz, 3 H), 3.36 (q, J = 6.91 Hz, 1 H), 3.76 (s, 3 H), 5.29 (qd, J = 7.07, 0.80 Hz, 1 H), 7.03 (s, 1 H). NMR spectrum of **17** ($CDCl_3$): δ 1.34 (d, J = 6.87 Hz, 3 H), 1.73 (d, J = 7.17 Hz, 3 H), 3.47 (qd, J = 6.87, 1.23 Hz, 1 H), 3.75 (s, 3 H), 5.46 (qd, J = 7.17 Hz, 1 H), 6.81 (s, 1 H).

The direct determination of the ee's of **16** and **17** was accomplished by adding aliquots of a $CDCl_3$ solution of tris[3-[(trifluoromethyl)hydroxymethylene]-(+)-camphorato]europium(III) [$Eu(thc)_3$] until base-line resolution of the ester methyl resonances was achieved. The results are given in Scheme I.

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Supplementary Material Available: Spectra of compounds synthesized (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.