Enantioselectivity of the Addition of Singlet and Triplet and the Chiral Rhodium-Complex-Catalyzed Addition of (Methoxycarbonyl)phenylcarbene to 1,3-Dimethylallene

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The reactions of enantioenriched 1,3-dimethylallene with singlet and triplet (methoxycarbonyl)-phenylcarbene, and with racemic 1,3-dimethylallene in the presence of a chiral rhodium catalyst, have been explored. Two major and two minor carbene adducts are formed, and the relative stereochemistry of ring and double bond substitution has been assigned. The enantioselectivity in the reaction with the singlet carbene is very high (∼95% in C_6D_6), whereas no enantioselectivity could be detected in the presence of the chiral rhodium catalyst. The results derived from the reaction with the triplet carbene could not be unambiguously interpreted.

Introduction

One of the major research areas in the author's laboratories over the past few years has been the study of the enantioselectivity of the [2 + 2], diradical intermediate cycloaddition reactions of enantioenriched 1,3-dimethylallene (13DMA) with acrylonitrile and methyl acrylate,[1] *N*-phenylmaleimide and dimethyl fumarate,[2] 1,1-dichloro-2,2-difluoroethene and 1,1-diphenylethene,[3] methyl propiolate,[4] and the unsymmetrically substituted 1-*tert*-butyl-3-methylallene with 1,1-dichloro-2,2-difluoroethene.[5] The enantioselectivities observed in these reactions range from very low to reasonably high values. Extensive molecular modeling calculations that have been carried out on the minimum-energy pathways of approach of the reactants and on the conformations of the diradical intermediates have indicated that as many as four independent low-energy reaction pathways may be involved in intermediate and product formation in some of the [2 + 2] cycloaddition reactions, each pathway differing in the degree of enantioselectivity. Each mode of approach leads directly to the formation of minimum-energy conformations of the diradical intermediates which are believed to undergo ring closure faster than rotation about the newly formed C−C bond.[1,2] The results of the molecular modeling calculations have indicated that the diradicophile approaches the least sterically hindered face of one of the double bonds of 13DMA with the more sterically demanding portions of the diradicophile being oriented opposite the methyl group on the double bond of the 13DMA undergoing attack. The results of a study on the asymmetric induction in intramolecular [2 + 2] photocycloadditions of optically active allenes tethered to enones and enoates have been recently reported, the levels of asymmetric induction being very high (93−100%).[6]

The addition of carbenes to allenes has received relatively little attention.[7] Creary has investigated the regioselectivity of the addition of singlet and triplet carbenes to 1,1-dimethylallene (11DMA),[8] with singlet carbenes undergoing addition to the dimethyl-substituted double bond of 11DMA, and the triplet carbenes undergoing ring closure of the diradical intermediates to produce adducts from addition to the nonsubstituted double bond of 11DMA. The latter regioselectivity is the same as that observed in the [2 + 2] diradical-intermediate cycloaddition reactions of 11DMA.[9] The enantioselectivity of the addition of a singlet or triplet carbene to a chiral allene appears not to have been investigated. Herein are described the results of stereochemical studies on the addition of singlet and triplet (methoxycarbonyl)-phenylcarbene (MPC) to enantioenriched 13DMA, and to racemic 13DMA in the presence of a chiral rhodium catalyst.

Results

Addition of Singlet MPC to Enantioenriched 13DMA. Freeze-degassed solutions of 13DMA and methyl diazophenylacetate (MDA) in $CDCl_3$ or C_6D_6 in sealed NMR tubes were irradiated with either a 275 W sunlamp (∼60 °C) or at 350 nm in a Rayonet photochemical reactor (∼35 °C). The irradiated solutions were periodically monitored by ^{1}H NMR spectroscopy, showing the clean formation of four carbene adducts (see Figure 1 which shows the ring methyl proton region in the ^{1}H NMR spectrum of the reaction mixture). At ∼35 °C a mixture of four adducts **1**−**4** (Scheme 1) was obtained in a ratio of 64:23:9:4, determined by the direct integration of the region of the NMR spectrum of the reaction mixture shown in Figure 1, which remained constant until the complete disappearance of the diazo precursor of the MPC. Irradiation at ∼60 °C with the sunlamp also initially produced the four adducts in a very similar ratio. However, on continued irradiation at ∼60 °C until the complete disappearance of the diazo compound, equilibration of the adducts was observed, ultimately resulting in a ratio of the four adducts of 43:5:43:9. Thermal equilibration in the dark of a mixture of the adducts at

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(8) Creary, X. *J. Am. Chem. Soc.* **1980**, *102*, 1611.
(9) Pasto, D. J.; Heid, R. F.; Warren, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 3676. Pasto, D. J.; Yang, S.-H. *J. Am. Chem. Soc.* **1984**, *106*, 152.

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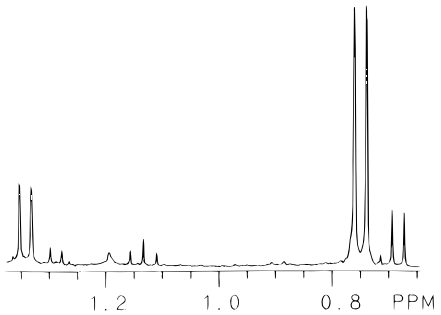
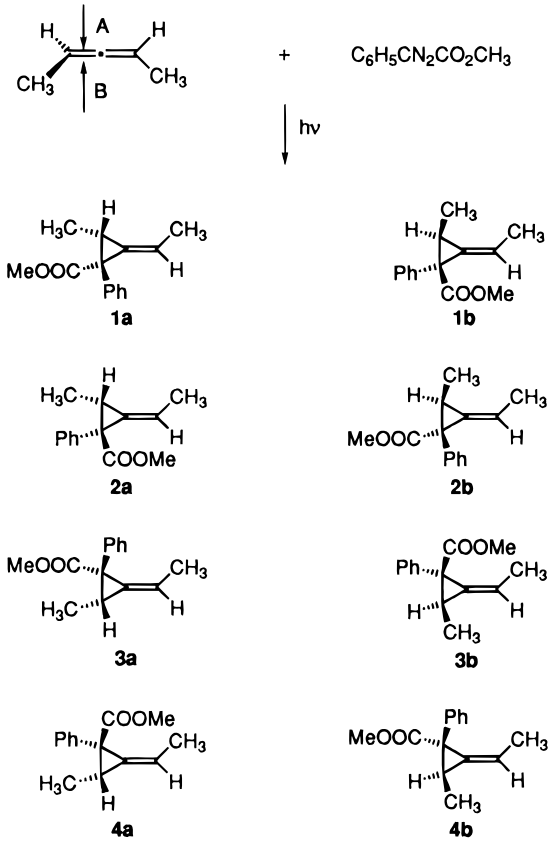


Figure 1. High-field methyl proton region of an initially formed reaction mixture of adducts **1**−**4**.

Scheme 1



80 °C resulted in a final ratio of 38:15:37:10. No thermal equilibration was observed to occur at 35 °C over a time period similar to that of the time of irradiation of the reaction mixture. Attempted separation of the mixture of adducts by flash chromatography and MPLC was unsuccessful. Attempted HPLC on silica gel gave only partial resolution of the mixture of adducts. HPLC on chiral (*R,R*)- and (*S,S*)-Whelk-O 1 columns[10] resulted in the separation of the four *d,l* pairs of adducts but did not resolve the individual enantiomers of the four *d,l* pairs of adducts. Integration of the chromatogram indicated a ratio of **1**−**4** of 72:14:3:1. The relative stereochemistries of the substituents on the three-membered ring and on the double bond, and the enantiomeric excesses of the carbene adducts have been assigned as described in the following paragraphs.

Earlier molecular-modeling based calculations indicated that the favored mode of attack at the central carbon atom of 13DMA in free radical addition reactions

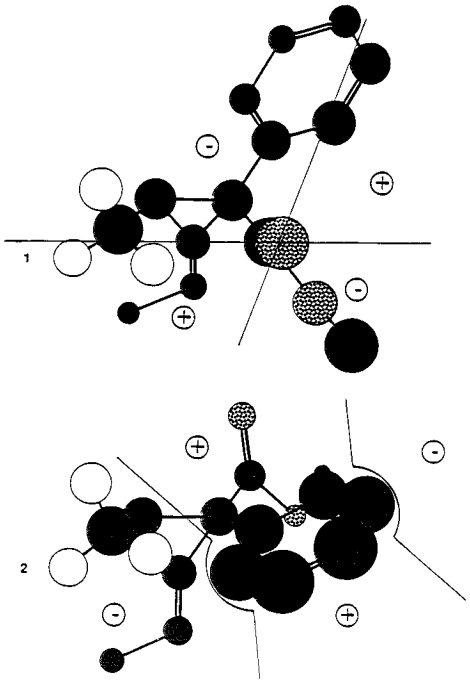


Figure 2. Lowest-energy conformations of the *cis*- and *trans*-ester,phenyl carbene adducts **1** and **2**.

and in the formation of diradicals in the [2 + 2] diradical intermediate cycloaddition reactions[1−6] had the largest group in the attaching reagent oriented away from the methyl group attached to the double bond undergoing attack, with the methyl group on the other double bond being oriented away from the attacking reagent. The application of these observations to the present reaction would suggest that the adducts having a *cis* relationship between the methyl and ester groups should be favored, with the exocyclic double bond possessing the *E*-stereochemistry.

Molecular modeling calculations carried out on the *cis*- and *trans*-structures **1** and **2** using the Spartan program[11] resulted in the lowest minimum-energy conformations shown in Figure 2. In the lowest-energy conformation of **1** the hydrogen atoms of the ring methyl group reside predominantly in the shielding region (+) of the carbonyl group, whereas in the lowest-energy conformation of **2** the hydrogen atoms of the ring methyl group reside in the deshielding region (−) of the aromatic ring. Thus, the methyl protons in **2** should appear at lower field than the protons of the ring methyl group of **1**. Accordingly, the two *d,l*-pairs of adducts possessing ring methyl chemical shifts of δ 1.31 and 1.37 are assigned to the *cis*-methyl,phenyl adducts **2** and **4**, and those possessing higher-field chemical shifts of δ 0.68 and 0.75 are assigned to the *cis*-methyl,ester adducts **1** and **3**.

Further support for these stereochemical assignments is provided by the relative retention times of the adducts on the (*R,R*)- and (*S,S*)-Whelk-O 1 columns.[10] The retention times of the four *d,l*-pairs of diastereoisomers were 10.1, 22.6, 18.1, and 19.8 min (in the sequence of the **1**−**4** ratio given above). Pirkle[12] and Welch[13] have rationalized the retention times of substrates on these columns in terms of the ability of a substrate molecule to fit into the "binding pocket" of the attached stationary

(10) Regis Technologies, Inc., 8210 Austin Avenue, P. O. Box 519, Morton Grove, IL 60053−0519.

(11) *Spartan*, Version 3.0, 1993, Wavefunction, Inc., 18401 Von Karman, Suite 370 Irvine, CA 92715.

(12) Pirkle, W. H. *J. Am. Chem. Soc.* **1966**, *88*, 1837.

(13) Welch, C. J. *J. Chromatogr., A* **1994**, *666*, 3.

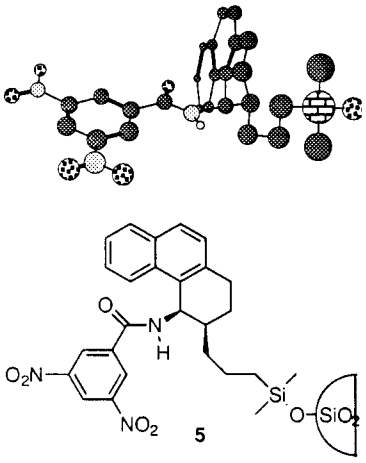


Figure 3. Representation of the "binding pocket" in the stationary phase of the Whelk-O 1 column.

phase **5** shown in Figure 3. The bottom of the "box" is the dinitrophenyl group which interacts in an attractive face-to-face π interaction with the phenyl group of the carbene adducts. The "side" of the box is represented by three fused rings which create a face-to-edge repulsive interaction with the phenyl groups in the carbene adducts. And, finally, the N−H within the "pocket" can hydrogen bond with the carbonyl group of the ester function in the adducts. An inspection of the fit of molecular models of **1**−**4** into a model of the binding site, shown in Figure 4, indicates the presence of interactions have been labeled large, small, and essentially nonexistent. The retention time on the column will be shortest for the carbene adduct having the most severe steric interactions with the binding pocket of the stationary phase, and longest retention time for the carbene adduct having the least steric interaction with the binding pocket of the stationary phase. Thus, the relative retention times observed on the chiral columns are in agreement with the stereochemical assignments based on the interpretation of the long-range shielding effects by the methoxycarbonyl and phenyl groups on the protons of the ring methyl group.

And, finally, the results of the thermal equilibration of the mixture of adducts **1**−**4** is consistent with the assigned ring stereochemistry. On thermal equilibration adducts **1** and **3** with the "smaller" ester group *cis* to the methyl group should dominate and be formed in essentially equal amounts. (It is considered that the vinyl methyl group is too distant to have a significant effect on the position of equlibrium of **1** and **3**.) The minor adducts **2** and **4** with with the "larger" phenyl group *cis* to the methyl group should be formed in lesser and essentially equal amounts.

The long-range coupling constants between the ring proton and the vinyl or the vinyl methyl protons, and the results of attempted NOE experiments, did not allow for the unique distinction between the *E*- and *Z*-stereoisomers. An attempt to correlate the chemical shifts of the vinyl and methyl protons with long-range shielding effects of the ester and phenyl groups similarly did not allow for a unique assignment of the stereochemistry about the double bond. The assignment of the stereochemistry about the exocyclic double bonds in the carbene adducts **1**−**4** is based on the results of our prior molecular modeling studies on the approach of a radicophile or radical to the central carbon of **13DMA** in which the favored mode of approach is opposite the largest group

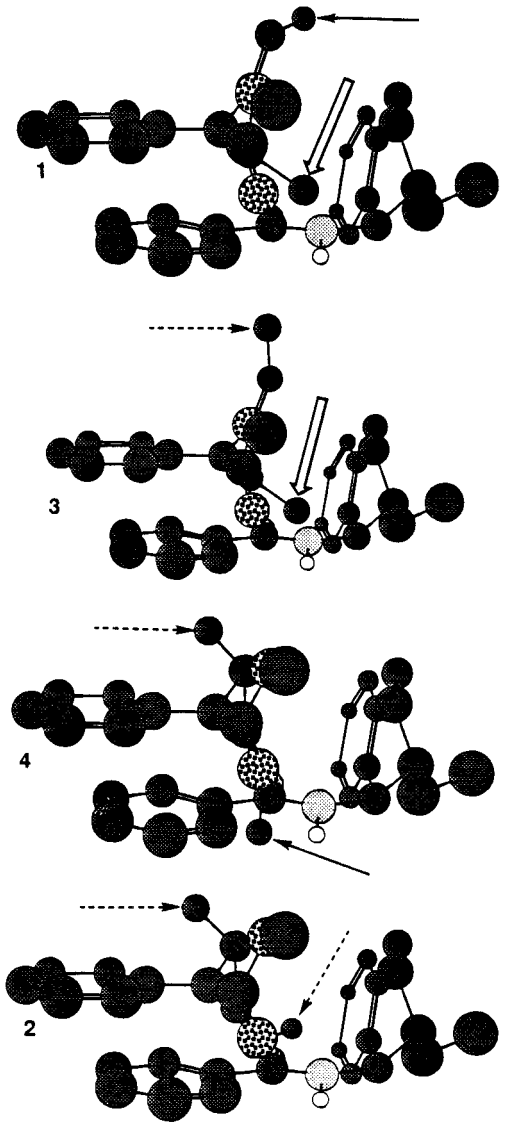


Figure 4. Representation of the steric interactions between the functions on the carbene adducts **1**−**4** and the functions in the "binding pocket" of the stationary phase of the Whelk-O 1 column (⟹ indicates large steric interactions, → indicates small steric interactions, ---> indicates essentially no steric interactions.

attached to other double bond which should result in the preferred formation of **1** and **2**.[6]

The enantiomeric excesses of the carbene adducts **1**−**3** were determined by the use of the chiral shift reagent tris[3-[(trifluoromethyl)hydroxymethylene]-(+)-camphorato]europium(III) [Eu(tfc)$_3$] in benzene-d_6.[14] Because of line broadening and the overlap of some of the peaks it was necessary to employ curve deconvolution of the ^{1}H NMR spectra in order to determine the enantiomeric excesses of the adducts. The data is provided in Table 1. (The enantiomeric excess of adduct **4** could not be determined because of the very small amount of **4** formed in the reaction, and the line broadening in the presence of the chiral shift reagent.) The analysis of the thermally

(14) Chemical methods were also attempted to determine the ee's of the carbene adducts, particularly adduct **4**, including conversion to the (*S*)-(−)-α-methylbenzylamides, the reduction of the mixture of adducts with lithium aluminum hydride to the corresponding alcohols (for chiral shift analysis) followed by conversion to the (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenyl esters (for use in ^{19}F NMR analysis), and the use of chiral solvating agents and cyclodextrin. None of these approaches were successful in resolving the pairs of enantiomers of **1**−**4**.

Table 1. Enantiomeric Excesses of Starting 13DMA and Derived Carbene Adducts 1−3

experiment	**1**[a]	**2**[a]	**3**[b]	**4**[b]
starting 13DMA	30.0	28.8	27.6	27.6
adduct **1**	*c*	*c*	23.9 (87)	27.4 (99)
adduct **2**	25.2 (84)	21.2 (74)	27.2 (99)	26.5 (96)
adduct **3**	21.2 (71)	20.7 (72)	22.6 (82)	25.4 (92)

[a] Reaction of triplet MPC in $CDCl_3$ as reaction solvent. [b] Reaction of singlet MPC in C_6D_6 as reaction solvent. [c] Enantiomerically related peaks could not be resolved in $CDCl_3$ solution.

equilibrated mixture of adducts **1**−**4** indicated that none of the adducts possessed any enantiomeric excess.

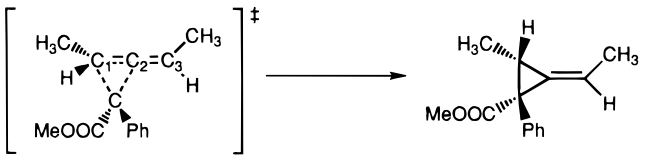
Reaction of 13DMA with Triplet MPC. The benzophenone-sensitized (7 mol equiv) photoinduced decomposition of MDA in the presence of (*S*)-(+)-13DMA in $CDCl_3$ produced a mixture of the carbene adducts **1**−**4** in a ratio of 62:23:8:7. The ee's of the carbene adducts **1**−**3** were determined using the chiral shift reagent, indicating that each of the adducts were formed with ~75% retention of ee.

Reaction of Racemic 13DMA with MDA in the Presence of Chiral Dirhodium(II) Tetrakis(methyl 2-pyrrolidone-5(*R*)-carboxylate (RPC).[15] The irradiation of a solution of racemic 13DMA and MDA in the presence of a catalytic amount of RPC produced a 35% yield of a mixture of the carbene adducts **1**−**4** in a ratio of 62:23:8:7. The ee analysis by use of the chiral shift reagent used in the above experiments indicated that there was no transfer of ee to the adducts **1**−**4**.

Discussion

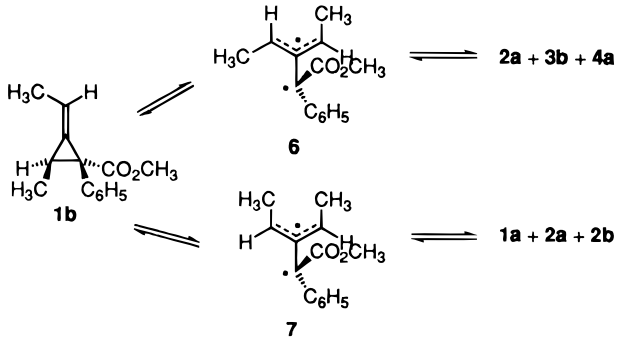
The transfer of ~90−95% ee of the enantiomerically enriched 13DMA to the carbene adducts **1**−**3** in the addition of singlet MPC represents a very high degree of enantioselectivity (stereoselectivity) in the formation of the transition structures for the addition of MPC to 13DMA. This suggests that the transition structures occur rather late along the reaction coordinate in which the degree of bond formation to form the substituted methylenecyclopropane system is quite advanced, and that the steric interactions between the functional groups on the MPC and the rather small methyl group on the 13DMA are quite large. This should have a significant impact on the ability to form highly enantioenriched substituted methylenecyclopropanes for synthetic or physical organic studies.

The observed thermal isomerization with concomitant racemization implies that each of the chiral carbene adducts can undergo reversible ring opening to form singlet diradicals which ultimately lead to racemization. This is shown in eq 1 illustrating the reversible ring opening of the chiral adduct **1b** to form the chiral diradical intermediate **6** and the achiral diradical intermediate **7**, the former being thermodynamically favored due to the methyl−methyl repulsion present in **7**. Ring closure of **6** to the bottom side of the left-hand portion of the allyl radical regenerates **1b**. Ring closure to the top side of the left-hand portion generates **2a**. Ring closure to the top and bottom sides of the right-hand portion of the allyl radical produces **3b** and **4a**, respectively. Thus, the ring opening to produce **6** leads only to isomerization but does not lead to racemization. Conversely, ring closure of **7** to the top left and top right ends of the allyl radical produce the enantiomers **1b** and **1a**, respectively,



1a

while closure to the bottom left and right ends of the allyl radical produces the enantiomers **2a** and **2b**, respectively. Similar ring opening processes can be illustrated for **2b**, **3a**, and **4a** (all possessing the same absolute configuration at the methyl-bearing ring carbon atom).



The situation is even further complicated by the possibility of rotation about the allyl-carbon−radical-carbon bond. Such rotational processes result in the generation of carbene adducts formally derived from the more sterically encumbered approach of the MPC to 13DMA to give the minor adducts **3** and **4**. Prior calculations carried out in the author's laboratories on the parent homotrimethylenemethane and methyl-substituted derivatives have indicate that a *syn*-methyl group on the allyl portion or on the appended alkyl-radical group substantially raises the energy barrier for rotation about the C−C bond connecting the allyl and homomethylene groups.[16] The energy barrier for rotation in **6** must be substantial, and it is expected that rotational isomerization in **6** probably does not occur.

The steric factors involved in the addition of triplet MPC to 13DMA should be very similar to that observed in the addition of free radicals and singlet carbenes to 13DMA and in the formation of the diradical intermediates formed in the [2 + 2] cycloaddition reactions of 13DMA. Thus, the formation of triplet **6** should be favored over the formation of triplet **7**. The ratio of the carbene adducts formed and the enantioselectivity depend critically on the relative rates of rotational isomerization within the triplet diradicals **6** and **7** versus the rate of intersystem crossing (ISC) to form the corresponding singlet diradical species which should undergo ring closure faster than rotational isomerization. If ISC and ring closure are rapid compared to the rate of rotational isomerization in **6**, the product distribution derived from the singlet and triplet MPC addition reactions via **6** to form **1** and **2** should be similar. On the other hand, if rotational isomerization in **7** is faster than ISC and ring closure, one should observe a difference in the ratios of **3**:**4**, and **1** plus **2** versus **3** plus **4**.

The results derived in the attempted generation and addition of triplet MPC to 13DMA do not allow for a

(15) Doyle, M. P; Protopopova, M. N. *J. Am. Chem. Soc.* **1992**, *114*, 1874. Doyle, M. P.; Protopopova, M. N. *J. Am. Chem. Soc.* **1992**, *114*, 2755. Doyle, M. P.; Winchester, W. R.; Hoorn, J. A. A.; Lynch, V.; Simonsen, S. H.; Gosh, R. *J. Am. Chem. Soc.* **1993**, *115*, 9968.

(16) Pasto, D. J.; Benn, D. C. *J. Org. Chem.* **1991**, *56*, 6209.

unique distinction between the various possibilities. The product distributions are too similar, and the slightly reduced enantioselectivity observed in the attempted triplet MPC addition reactions are not sufficient to allow for an unambiguous interpretation. It is most reasonable to conclude that the enantioselectivity observed in the attempted triplet generation and addition of MPC to enantioenriched 13DMA might be due to a competitive generation of the singlet MPC which adds to the 13DMA in a highly enantioselective fashion, the loss in ee being due to the minor addition of triplet MPC to 13DMA along with some contribution of thermal racemization of the enantioenriched adducts formed by the addition of singlet MPC to 13DMA.

The results derived from the attempted chiral rhodium complex RPC-catalyzed additon of MPC to racemic 13DMA is some what surprising, no enantioselectivity being observed. This is in contrast to the high degree of enantioselectivity observed in similar rhodium-complex-catalyzed carbene additions to substituted alkenes.[15] The reason(s) for this could be that, although substituted allenes are "reputedly" much more reactive that similarly substituted alkenes,[17] the FMOs of alkyl-substituted allenes are higher and lower in energy than those of similar alkyl-substituted alkenes[18] thus reducing the effective ability of 13DMA to complex with the rhodium catalyst.

Conclusions

The results of the present study have shown that the addition of singlet carbenes to an enantioenriched chiral allene can occur with a very high degree of enantioselectivity. Definitive results as to the enantioselectivity of the addition of triplet carbenes to a chiral allene were not obtained. The catalyzed addition of a carbene by a chiral rhodium complex to a racemic chiral allene suprisingly showed no enantioselectivity.

Experimental Section

Preparation of (*S*)-(+)-1,3-Dimethylallene. Enantioenriched 1,3-dimethylallene was prepared as described earlier in the literature.[19] The ee's of the samples of enantioenriched 1,3-dimethylallene were determined by polarometric methods.[20]

Reaction of Singlet (Methoxycarbonyl)phenylcarbene with Enantioenriched 1,3-Dimethylallene. Freeze-degassed solutions of (*S*)-(+)-1,3-dimethylallene (0.28 M) and 2 mol equiv of methyl α-diazophenylacetate[21] (MDA) in $CDCl_3$ or C_6D_6 in sealed NMR tubes were irradiated either by a 275 W GE sunlamp (~60 °C) or in a Rayonet photochemical reactor at 350 nm (~35 °C). The solutions were periodically analyzed by ^{1}H NMR spectroscopy, the irradiations being continued until the disappearance of the MDA. The solvent was then removed under reduced pressure and the residue was subjected to medium-pressure liquid chromatography on silica gel using Skellysolve F−methylene chloride as eluent. An inseparable mixture of the adducts **1**−**4** was obtained in ~43% yield as a pale yellow solid. ^{1}H NMR ($CDCl_3$, characteristic resolvable peaks only are given, see also Figure 1): δ 0.68 (d, J = 6.4 Hz), 0.75 (d, J = 6.4 Hz), 1.29 (d, J = 6.2 Hz), 1.34 (d, J = 6.4 Hz), 1.80 (dd, J = 6.7, 2.2 Hz), 1.83 (dd, J = 6.7, 2.1 Hz), 1.90 (dd, J = 6.7, 2.2 Hz), 1.90 (dd, J = 6.7, 2.2), 1.92 (dd, J = 6.7, 1.7 Hz) 1.99 (dq, J = 2.2, 6.4 Hz), 2.57 (dq, J = 2.2, 6.4 Hz), 3.57 (s), 3.58 (s), 3.60 (s), 5.71 (dq, J = 2.4, 6.7 Hz), 5.96 (dq, J = 2.1, 6.7 Hz), 6.06 (dq, J = 2.4, 6.7 Hz). HRMS (on mixture) Calcd for $C_{14}H_{16}O_2$: m/z 216.1150. Found: m/z 216.1149.

Determination of the Enantiomeric Excesses of the Carbene Adducts 1−4. To the crude reaction mixture formed in C_6D_6 was added incremental amounts of tris[3-[(trifluoromethyl)hydroxymethylene]-(+)-camphorato]europium-(III) dissolved in C_6D_6, and the ^{1}H NMR spectra were recorded. Extensive line broadening occurred, but by the use of deconvolution techniques the ee's of the adducts **1**−**3** could be determined. The results are given in Table 1.

Thermal Equilibration of the Mixture of Carbene Adducts. A solution of the initially formed mixture of carbene adducts **1**−**4** in a sealed NMR tube was heated in a sand bath at 40 and 60 °C. The ^{1}H NMR spectra of the samples were periodically recorded. The rate of isomerization at 40 °C was very slow and was not taken to completion. After 24 days the sample had undergone ~50% equilibration. The sample was further heated at 80 °C until no further change in the ratio of **1**−**4** was observed given a final ratio 38:15:37:10.

Irradiation of a Mixture of 1,3-Dimethylallene and MDA in the Presence of Benzophenone. A solution of MDA, (*S*)-(+)-13DMA, and 7 mol equiv of benzophenone dissolved in $CDCl_3$ was irradiated with a 275 W GE sunlamp until the complete dissapearance of the MDA as determined by periodic NMR spectroscopic analysis (~12 h). Attempted chromatographic separation of the adducts from the benzophenone could not be successully achieved.

The reaction mixture was dissolved in 20 mL of methanol and subjected to reduction with 1.1 equiv (based on the amount of benzophenone present) of sodium borohydride at 25 °C for 1 h. The reaction mixture was quenched by the addition of potassium carbonate, and the methanol was removed under reduced pressure. The residue was extracted with diethyl ether, and the extract was dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was subjected to medium-pressure liquid chromatography on silica gel using Skellysolve F−methylene chloride as eluent. The ee's of the adducts **1**−**4** was determined as described above. The results are given in Table 1.

Reaction of MDA with Racemic (*S*)-(+)-13DMA in the Presence of Dirhodium(II) Tetrakis(methyl 2-pyrrolidone-5(R)-carboxylate) (RPC). A freeze-degassed solution of MDA, racemic 13DMA, and 2 mol equiv of the chiral dirhodium complex RPC in $CDCl_3$ was irradiated in a sealed NMR tube until the complete diasppearance of the MDA. The solvent was removed under reduced pressure, and the residue was subjected to medium-pressure liquid chromatography on silica gel using Skellysolve F−methylene chloride as eluent. Ee analysis as described above indicated no ee in any of the adducts **1**−**4**.

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(17) The higher degree of reactivity of substituted allenes versus alkenes is almost always due to the formation allyl intermediates which enjoy the extra stabilization of the allyl π system relative to the lack of such stabilization in vinyl intermediates (see ref 18).

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