# Exceptionally High Trans (Anti) Stereoselectivity in Catalytic Cyclopropanation Reactions

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Abstract: Exceptionally high trans (anti) stereoselectivities are obtained in rhodium(II) carboxylate and carboxamide catalyzed alkene cyclopropanation reactions with 2,6-di-tert-butyl-4-methylphenyl diazoacetate (BDA). With monosubstituted ethylenes, use of rhodium(II) acetamide provides a 10–20% increase in the relative yield of the trans-disubstituted cyclopropane. Compared to results from rhodium(II) acetate catalyzed reactions with ethyl diazoacetate, the selectivity enhancement achieved with BDA corresponds to energy differences of between 1.0 and 2.0 kcal/mol and, in many cases, provides greater than 95% relative yield of the trans (anti) isomer. Intermediate selectivities are obtained with 2,3,4-trimethyl-3-pentyl diazoacetate (ODA) and 3-isopropyl-2-methyl-3-heptyl diazoacetate (UDA). Alkenes such as 2,5-dimethyl-2,4-hexadiene that are normally resistant to changes in their trans/cis cyclopropane product ratio by either catalyst modification or the use of alkyl diazoacetates such as ODA or UDA undergo highly selective cyclopropanation with BDA. Relative reactivities for cyclopropanation of selected alkenes extend over 3 orders of magnitude for reactions with BDA, and they suggest the extent of regioselectivity control in reactions with dienes and polyenes. Catalyst influences on reactivity and stereoselectivity clearly show the advantages of dirhodium(II) tetrakis(acetamide) over rhodium(II) carboxylates for the production of the trans (anti) cyclopropane isomer and for highly regioselective cyclopropanation reactions with BDA.

Among all of the catalysts that have been developed for carbene addition to multiple bonds, rhodium(II) carboxylates are the most effective for intermolecular reactions that employ diazo carbonyl compounds.[1] Alkenes ranging from enol ethers and acetates through monoalkenes to dienes and trienes,[2-6] but not α,β-unsaturated carbonyl compounds or nitriles,[7] undergo Rh₂-(OAc)₄-catalyzed cyclopropanation (eq 1) in high yield with
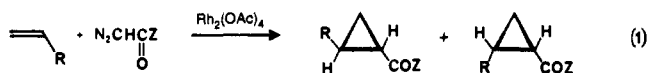

minimum interference from normally competitive carbenoid dimerization.[8] However, stereoselectivities for these transformations are low. In reactions with monosubstituted olefins, trans/cis cyclopropane ratios rarely exceed 2, and even cis-disubstituted alkenes exhibit anti/syn isomer ratios that are generally less than 4.[3-5]

We have recently reported[9] that enhancement of trans (anti) stereoselectivities in cyclopropanation reactions could be achieved with the use of rhodium(II) acetamide[10] as the catalyst and 2,3,4-trimethyl-3-pentyl diazoacetate (ODA) as the carbenoid precursor. The electronic influence of the acetamide substituents in Rh₂(acam)₄ apparently increases the stability of the intermediate metal carbene, thereby effecting a closer approach of the unsaturated substrate to the electrophilic carbenoid center.[11] The larger steric bulk of the diazo ester favors the orientation of reactants that leads to the trans (anti) isomer. Still, the combined influence of these modifications is limited. They increase the

relative percentages of the thermodynamically more stable cyclopropane isomer from 62% to 87% (with styrene) and from 79% to 92% (with cyclohexene),[9] which corresponds to only a 0.6–0.8 kcal/mol energy difference from stereoselectivities achieved with Rh₂(OAc)₄ and ethyl diazoacetate (EDA). We now wish to report the optimization of this methodology that allows catalytic cyclopropanation to be achieved with trans (anti) stereoselectivities that are greater than 90% and, in many cases, exceed 95%.

Results

Influence of Diazo Esters. On the basis of the enhancement in relative yields of trans (anti) cyclopropane stereoisomers obtained with 2,3,4-trimethyl-3-pentyl diazoacetate (ODA),[9,12] two additional diazoacetates with bulky ester appendages, 3-isopropyl-2-methyl-3-heptyl diazoacetate (UDA)[12] and 2,6-di-tert-butyl-4-methylphenyl diazoacetate (BDA), were prepared in order to determine their influence on stereoselectivity. Both ODA and

ODA   UDA   BDA
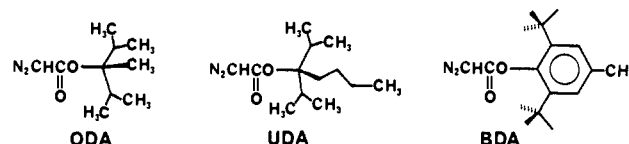
UDA were conveniently synthesized from the corresponding alcohols in three steps by diketene addition,[13,14] diazo transfer,[15] and deacylation,[16] and ODA was sufficiently stable to be purified by low-temperature distillation. The synthesis of BDA was accomplished in two steps by performing diketene addition to 2,6-di-tert-butyl-4-methylphenol (BHT) in the presence of methanesulfonyl azide (eq 2) with significant advantages in product
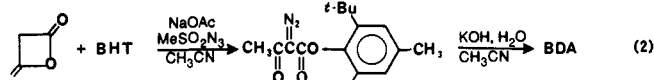
yield and purity over the sequential three-step process. The relatively high melting point of BDA (153 °C) suggests its exceptional stability.

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Table I. Stereoselectivities in $Rh_2(OAc)_4$-Catalyzed Cyclopropanation Reactions with Representative Alkenes[a]

	% trans (anti)[b]			
alkene	EDA (1)[c]	ODA (2)[d]	UDA (3)[e]	BDA (4)
ethyl vinyl ether (a)	62	67 (92)	70 (88)	71 (96)
1-hexene (b)	60	71 (90)	74 (87)	75 (93)
styrene (c)	62	71 (94)	73 (87)	84 (94)
3,3-dimethyl-1-butene (d)	75	84 (89)	89 (84)	93 (92)
cyclopentene (e)	72		97 (79)	69 (52)[f]
cyclohexene (f)	79	90 (86)	92 (81)	91 (60)[g]
bicyclo[2.2.1]hept-2-ene (g)	67	76 (90)	82 (84)	95 (92)
dihydropyran (h)	87		85 (88)	97 (92)
2-methyl-2-butene (i)	60	64 (86)	65 (81)	96 (89)
2,5-dimethyl-2,4-hexadiene (j)	62	65 (88)	60 (73)	94 (88)

[a] Reactions were performed at room temperature with 1.0 mol % of the catalyst, based on the diazo compound, and a 10-fold molar excess of the alkene. [b] Yield of cyclopropane products prior to chromatographic purification in parentheses. [c] Data from ref 3. [d] Stereoselectivities are consistent with those reported in ref 9. Only trace amounts of lactone 7 were observed. [e] Lactones 8 and 9 were formed competitively (5–18% yield). [f] Complex mixture consisting of cyclopropane derivatives (34%) and insertion products (66%). [g] Complex mixture consisting of cyclopropane derivatives (14%) and insertion products (86%).

Cyclopropanation reactions were performed by controlled addition of the diazo ester to the combination of alkene and 1.0 mol % $Rh_2(OAc)_4$ in dichloromethane at room temperature. A 10-fold excess of the alkene was employed to obtain uniformity in yield determinations by minimizing competitive carbene dimer formation. However, comparable product yields could be obtained in reactions with the most reactive alkenes by using only a 2-fold excess of alkene and adjusting the rate of addition. Stereoselectivities in cyclopropane formation from $Rh_2(OAc)_4$-catalyzed reactions of EDA, ODA, UDA, and BDA with a representative series of mono-, di-, and trisubstituted ethylenes are reported in Table I. Stereoisomers were identified by their characteristic NMR spectra, from which coupling constants, especially for the hydrogen on carbon adjacent to the carboxylate group, revealed stereochemistry.[3,8]

As expected, the change in cyclopropanation selectivities between EDA and ODA is greater than that between ODA and UDA. Compared to the use of tert-butyl diazoacetate,[17] use of ODA has a greater influence on stereoselectivity, and even though far removed from the reaction center, the n-butyl group of UDA has a measurable influence on the relative percentage of the trans (anti) isomer compared to the methyl group of ODA. Perhaps the most surprising result, however, is the relative absence of stereoselectivity enhancement in reactions of either ODA or UDA with the trisubstituted ethylenes 2-methyl-2-butene and 2,5-dimethyl-2,4-hexadiene.

The phenolic ester BDA, whose development was influenced by the enhanced stereoselection in aldol condensation reactions observed by Heathcock and co-workers with BHT esters,[18] is superior to either ODA or UDA for stereoselectivity enhancement in cyclopropanation reactions. Relative yields of the trans (anti) stereoisomers (4) are the highest yet achieved in catalytic reactions, and even the normally resistant trisubstituted ethylenes are very responsive to the steric bulk of the phenolic attachment. Indeed, the exceptional selectivity obtained in the preparation of 4j makes this the method of choice for the synthesis of trans chrysanthemic acid derivatives.[19] However, cyclohexene gave abnormally low yields of cyclopropane products with BDA due to competitive formation of its apparent allylic insertion product 5. Similarly, 6 was formed in reactions with cyclopentene, but the analogous product from reactions with dihydropyran was formed in low yield (<3%).

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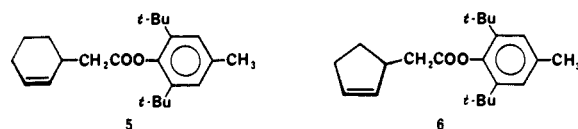

Except with cyclopentene and cyclohexene, product yields are uniformly high for cyclopropanation reactions of BDA, and competitive carbenoid dimerization of the diazo ester is less important in reactions with BDA than in reactions with EDA.[20] Azine production is generally not observed in catalytic reactions of EDA or of ODA and UDA, but it is the major competing process in catalytic reactions performed with BDA, albeit normally of minor importance. Restricted access to the diazo carbon apparently limits carbene dimer formation.

Unlike cyclopropane products formed with ODA and UDA, which underwent partial decomposition upon attempted distillation, those formed from BDA were thermally stable under a variety of experimental conditions. Like the 2,6-di-tert-butyl-4-methylphenyl esters examined by Heathcock and co-workers, the cyclopropane products formed from BDA were resistant to hydrolysis, but those prepared from monosubstituted alkenes could be converted to their corresponding carbinol derivatives by reduction with $LiAlH_4$ in tetrahydrofuran. Interestingly, the reduction of a mixture of the BHT cis- and trans-2-n-butylcyclopropanecarboxylates by $LiAlH_4$ in ether exhibited exceptional selectivity for the trans ester. Nearly pure trans-2-n-butylcyclopropanemethanol and pure BHT cis-2-n-butylcyclopropanecarboxylate were formed in refluxing ether from a BHT ester mixture consisting of 2 parts of the trans isomer and 1 part of the cis isomer (eq 3). Only after 72 h in refluxing THF was $LiAlH_4$ reduction of the cis-cyclopropanecarboxylate ester virtually complete.

$$(3)$$
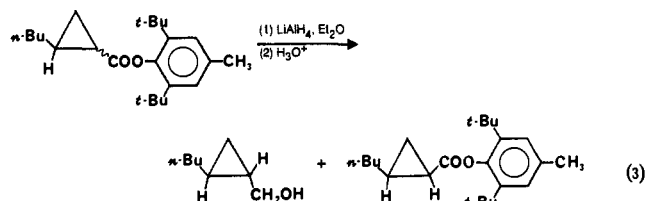
Diazo amides are potentially more suitable for trans (anti) stereoselection in cyclopropanation reactions because of the closer proximity of N-alkyl substituents to the electrophilic carbenoid center. For example, N,N-dimethyldiazoacetamide offers greater selectivity in $Rh_2(OAc)_4$-catalyzed reactions than does EDA:[9] styrene (69% trans), ethyl vinyl ether (64% trans), and cyclohexene (94% anti). However, product yields decrease with decreasing olefin reactivity: ethyl vinyl ether (82%) > styrene (47%) > cyclohexene (21%). In addition, with N-alkyl substituents larger than methyl, the carbenoid reagents are subject to intramolecular C–H insertion.[21] In $Rh_2(OAc)_4$-catalyzed reactions of styrene with N,N-diisopropyldiazoacetamide, for example, the trans-2-phenylcyclopropanecarboxamide isomer was obtained in 98% relative yield, but the actual yield of cyclopropane products could not be made to exceed 53% because of competitive intramolecular C–H insertion (eq 4). Reactions of N,N-diisopropyldiazoacet-

$$(4)$$
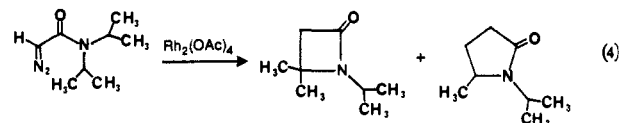
amide in the presence of cyclohexene yielded only the intramolecular C–H insertion products. Similar insertion processes were unimportant for $Rh_2(OAc)_4$-catalyzed reactions with ODA and BDA performed in the presence of alkenes.

Influence of the Catalyst. A variety of dirhodium(II) compounds with differing electronic influences imparted on the rho-

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Table II. Influence of Dirhodium(II) Catalysts on Ethyl Diazoacetate Cyclopropanation Stereoselectivities[a]

| catalyst	% trans (anti)[b]		
	ethyl vinyl ether	styrene	cyclohexene
Rh₂(NHCOCH₃)₄	72	68	89
Rh₂(OOCCH₃)₄	62	62	79
Rh₂(OOCC₃H₇)₄	60	60	77
Rh₂(NHCOCF₃)₄	62	59	74
Rh₂(OCSCH₃)₄	60	62	75
Rh₂(OOCCF₃)₄	59	56	67
Rh₂(OOCC₃F₇)₄[c]	57	52	66

[a]Reactions were performed at room temperature with 1.0 mol % of the catalyst, based on the diazo compound, and a 10-fold molar excess of the alkene. [b]Product yields ranged from 65% to 98% with median yields of 82-88%. [c]Percent trans isomer from reactions with 3,3-dimethyl-1-butene (60%), bicyclo[2.2.1]hept-2-ene (59%), 1-hexene (55%), and 2,5-dimethyl-2,4-hexadiene (58%).

dium(II) center by its ligands were prepared to develop one that would exhibit, relative to Rh₂(OAc)₄, increased carbenoid stereoselectivity in cyclopropanation reactions. Selectivity evaluations were made from reactions of EDA with a selection of olefins that provide a range of reactivities toward carbenoid addition, and the results of this survey are presented in Table II. As is evident from these results, rhodium(II) acetamide (acam) provides the highest and rhodium(II) perfluorobutyrate (pfb) the lowest trans (anti) cyclopropanation selectivities.

Rhodium(II) acetamide has previously been prepared as a mixture of the tetraacetamide with varying amounts of Rh₂-(acam)₃(OAc) and Rh₂(acam)₂(OAc)₂ by treating Rh₂(OAc)₄ in a melt of acetamide.[10a] Even when acetamide was employed in 100-150-fold molar excess over Rh₂(OAc)₄ and the procedure repeated several times, pure Rh₂(acam)₄ could be obtained only by HPLC separation. We have repeated these experiments, with Rh₂(OAc)₄ and with the more labile Rh₂(OOCCF₃)₄ as reactants,[22a] and obtained similar results. However, when this synthesis was performed in refluxing chlorobenzene under conditions where acetic acid was trapped by sodium carbonate in a Soxhlet extraction apparatus, pure Rh₂(acam)₄ was obtained without any evident trace of Rh₂(acam)₃(OAc). Spectral analysis confirmed that the tetraacetamide compound had the cis geometry.[10,23]

Stereoselectivities in cyclopropane formation from Rh₂-(acam)₄-catalyzed reactions of EDA, ODA, UDA, and BDA with a representative series of alkenes are reported in Table III. Even with EDA, Rh₂(acam)₄ increases the relative yield of the trans (anti) isomer, compared to that obtained with Rh₂(OAc)₄, by as much as 15%, and the use of ODA provides additional enhancement. Further improvements are seen with UDA, but it is BDA from which the highest trans (anti) stereoselectivities are achieved in catalytic cyclopropanation reactions.

With Rh₂(acam)₄ as the catalyst, products from competitive intramolecular carbon–hydrogen insertion of ODA and UDA are observed, especially in reactions performed with 1-hexene, cyclohexene, and 2,5-dimethyl-2,4-hexadiene. With ODA as the reactant, lactone 7 is formed, whereas with UDA both 8 and 9 are produced (8/9 = 2.0). Their yield is dependent on the alkene
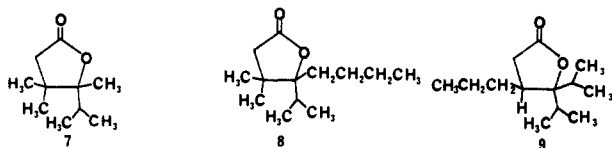
employed, but increasing the concentration of the alkene lessens the relative importance of this competing process. The scope of this intramolecular process is currently under investigation and will be described in a subsequent publication.

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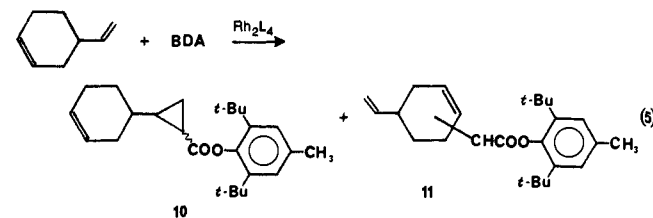(23) Ahsan, M. Q.; Bernal, I.; Bear, J. L. *Inorg. Chem. Acta* **1986**, *115*, 135.

Table III. Stereoselectivities in Rh₂(acac)₄-Catalyzed Cyclopropanation Reactions with Representative Alkenes[a]

alkene	% trans (anti)[b]			
	EDA (1)[c]	ODA (2)[d]	UDA (3)[e]	BDA (4)
ethyl vinyl ether (a)	72	80 (86)		85 (96)
1-hexene (b)	63	81 (84)	83 (55)	93 (88)
styrene (c)	68	87 (81)	93 (78)	98 (90)
3,3-dimethyl-1-butene (d)	83	89 (80)		99 (90)
cyclohexene (f)	89	92 (75)	96 (39)	92 (21)[f]
bicyclo[2.2.1]hept-2-ene (g)	82	83 (86)	86 (63)	92 (78)
2-methyl-2-butene (i)	58	66 (72)	65 (67)	
2,5-dimethyl-2,4-hexadiene (j)	60	59 (75)	60 (62)	98 (75)

[a]Reactions were performed at room temperature with 1.0 mol % of the catalyst, based on the diazo compound, and a 10-fold molar excess of the alkene. [b]Product yield in parentheses. [c]Data from ref 9. [d]Lactone 7 was produced in 8-22% yield. [e]Lactones 8 and 9 were formed in 15-50% yield. [f]Complex mixture consisting of cyclopropane derivatives (18%) and insertion products (82%).

Relative Reactivities. To determine if the increases in stereoselectivity occur with changes in reactivity, experiments were performed with pairs of alkenes, normally including 1-hexene, to obtain relative reactivities for interception of the intermediate metal carbene, and these results are reported in Table IV. Prior determinations that were limited to cyclopropanation reactions with EDA catalyzed by Rh₂(OAc)₄[11] showed that aliphatic monosubstituted alkenes were less reactive than di- or trisubstituted alkenes and that vinyl ethers were more reactive than styrene, which, in turn, was more reactive than 1-hexene. This same reactivity scale, although moderately expanded, is observed in reactions of EDA catalyzed by Rh₂(acam)₄. With either ODA or BDA, however, 2,5-dimethyl-2,4-hexadiene is no longer more reactive than 1-hexene, and cyclohexene is considerably less reactive than 1-hexene in cyclopropanation reactions performed with BDA. Cross-checks of relative reactivity values with different pairs of alkenes were performed to certify the validity of these numbers.

These relative reactivities were used to evaluate the potential of BDA for regioselective cyclopropanation of 4-vinylcyclohexene (eq 5). On the basis of the data in Table IV for Rh₂(OAc)₄-

catalyzed reactions of BDA, the expected distribution of products would be 93% 10 and 7% 11; the actual distribution was 93% 10 (83% trans, 17% cis) and 7% 11. Similarly, with Rh₂(acam)₄ the product distribution from the reaction of BDA with 4-vinylcyclohexene was 98% 10 and 2% 11, with a stereoisomer ratio for 10 of 67 (trans/cis).

Discussion

Stereoselectivities obtained by increasing the steric bulk of diazoacetate esters are consistent with the mechanism for cyclopropanation that is outlined in Scheme I. As previously reported,[1a,4,11] stabilization of the transition states leading to cyclopropane products by association of the ester carbonyl oxygen with the developing electropositive center of the reacting alkene accounts for the preferential trans (anti) stereoselectivity that is observed in intermolecular cyclopropanation reactions of diazo esters, as well as for dihydrofuran formation in reactions of vinyl ethers with diazo ketones[11,24] and for the apparent allylic carbon–hydrogen insertion of diazomalonate esters with alkenes.[1a,25]

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Table IV. Relative Reactivities in $Rh_2(OAc)_4$- and $Rh_2(acam)_4$-Catalyzed Cyclopropanation Reactions of Representative Alkenes with EDA, ODA, and BDA

	relative reactivities[a]					
	EDA		ODA		BDA	
alkene	$Rh_2(OAc)_4$	$Rh_2(acam)_4$	$Rh_2(OAc)_4$	$Rh_2(acam)_4$	$Rh_2(OAc)_4$	$Rh_2(acam)_4$
ethyl vinyl ether	8.3	15[b]	9.0	19[b]	13	20[b]
styrene	3.5	10	1.9	3.9	3.8	14
1-hexene	1.0	1.0	1.0	1.0	1.0	1.0
2,5-dimethyl-2,4-hexadiene	2.1	2.0	0.26	0.29	0.28	0.090
cyclohexene	2.5	1.0	1.2	0.73	0.078[c]	0.022[c]

[a] Reactions performed in dichloromethane at 25 °C [with $Rh_2(OAc)_4$] or at reflux [with $Rh_2(acam)_4$] with a 10-fold molar excess of each alkene and 1.0 mol % of the catalyst. [b] Because of its volatility, ethyl vinyl ether was replaced by *n*-butyl vinyl ether in these experiments. [c] Calculation includes cyclopropane products and the insertion product 5.

Table V. Relative Reactivities for Trans (Anti) and Cis (Syn) Cyclopropanation with EDA, ODA, and BDA Catalyzed by $Rh_2(OAc)_4$ and $Rh_2(acam)_4$

	relative reactivities[a]											
	EDA				ODA				BDA			
	$Rh_2(OAc)_4$		$Rh_2(acam)_4$		$Rh_2(OAc)_4$		$Rh_2(acam)_4$		$Rh_2(OAc)_4$		$Rh_2(acam)_4$	
alkene	trans (anti)	cis (syn)	trans (anti)	cis (syn)	trans (anti)	cis (syn)	trans (anti)	cis (syn)	trans (anti)	cis (syn)	trans (anti)	cis (syn)
ethyl vinyl ether	8.6	5.3	17	6.7	8.5	4.2	19	4.6	12	5.0	18	3.2
styrene	3.6	2.2	11	5.1	1.9	0.78	4.2	0.62	4.3	0.81	15	0.30
1-hexene	1.0	0.67	1.0	0.59	1.0	0.41	1.0	0.23	1.0	0.33	1.0	0.075
2,5-dimethyl-2,4-hexadiene	2.2	1.3	1.9	1.3	0.24	0.13	0.21	0.15	0.35	0.022	0.095	0.0019
cyclohexene[b]	3.3	0.83	1.4	0.19	1.5	0.17	0.83	0.072	0.013	0.0012	0.0039	0.0003

[a] Data calculated from Table IV. The relative reactivities for trans cyclopropane formation from 1-hexene were set at 1.0, and relative reactivities for cis cyclopropane formation for 1-hexene were calculated from the observed stereoselectivities. Relative reactivities for cyclopropanation of alkenes were determined from the formula [relative reactivity of alkene (from Table IV)] × [sum of relative reactivities for cyclopropanation of 1-hexene (Table V)] × [mole fraction of stereoisomer from cyclopropanation of alkene (from Tables I and III)]. [b] Values for reactions with BDA are dependent on the relative yield of 5, and relative reactivities for apparent insertion are approximately 0.081 with $Rh_2(OAc)_4$ and 0.016 with Rh_2-(acam)$_4$.

Scheme I
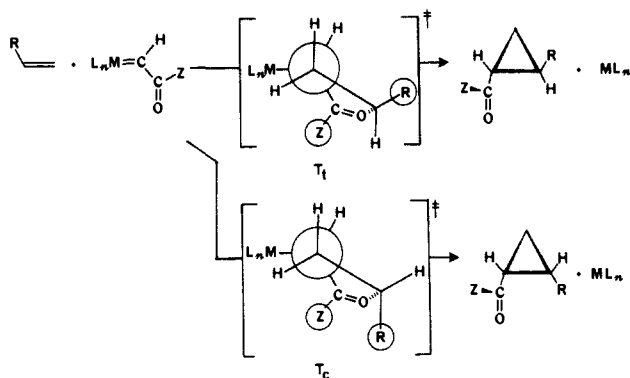
Increasing the size of Z (Scheme I) favors the transition state leading to the trans cyclopropane isomer. This effect is more pronounced in reactions with less electron rich alkenes (compare 1-hexene with ethyl vinyl ether), presumably because they require a closer approach to the carbenoid center in the transition state for cyclopropanation. The same can be said for the influence of the catalyst; use of rhodium(II) acetamide provides greater selectivity in intermolecular cyclopropanation reactions because its derivative metal carbene complexes are more stable than those derived from rhodium(II) acetate, which, in turn, are more stable than those formed from rhodium(II) perfluorobutyrate.

Increases in trans (anti) selectivity for cyclopropanation of alkenes are a function of their substituents. Cis-disubstituted alkenes such as cyclohexene are most responsive to changes in the steric bulk of the diazo ester, and trisubstituted alkenes such as 2,5-dimethyl-2,4-hexadiene are least responsive. However, electronic influences governing closeness of approach of the alkene to the carbene center, influenced both by alkene substituents and by ligands of the catalyst, are of comparable importance. Calculation of the relative rates for cyclopropanation yielding trans (anti) and cis (syn) isomers, each based upon the formation of the trans cyclopropane product from reactions with 1-hexene (Table V), provides a guide to these influences.

Relative reactivities for formation of trans (anti) cyclopropane isomers are of comparable magnitude for reactions with EDA, and their breadth of values increases by only a small degree in reactions performed with ODA. With BDA, however, relative reactivities for trans (anti) cyclopropanation of the selected series of alkenes vary by over 3 orders of magnitude, presumably because of steric constraints placed upon alkene orientation by the reactive carbene in the transition state. Rhodium(II) acetamide expands the range of values, relative to rhodium(II) acetate, in each series by a factor of 2 or more. Among monosubstituted alkenes, however, reactivities are relatively invariant with respect to the size of the diazo compound.

Relative reactivities for formation of the cis (syn) isomer, on the other hand, generally exhibit substantial changes with the increased size of the diazo ester, and these changes are most pronounced with $Rh_2(acam)_4$ as the catalyst. Nowhere are these influences more evident than in reactions with 2,5-dimethyl-2,4-hexadiene, where a 10-fold decrease in reactivity is observed between EDA and ODA and another 80-fold decrease occurs between ODA and BDA. Even the reactivity of styrene for formation of its cis-disubstituted cyclopropane derivative decreases from 5.1 to 0.30 relative to 1-hexene trans reactivity.

The formation of allylic insertion products is the dominant pathway in reactions of cyclohexene with BDA. Reactivities for insertion relative to those for cyclopropanation are 2.7 with $Rh_2(OAc)_4$ and 2.8 with $Rh_2(acam)_4$. A similar process has been observed in copper-catalyzed reactions of cyclohexene with diazomalonate esters,[26] but its contribution to total product formation was minor. A few additional examples have been reported,[11,24a] but none in yields as high as those encountered from reactions

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of BDA with cyclohexene. This process has the appearance of an intermolecular addition–elimination reaction,[1a] but further investigations are required to confirm the mechanism.

Not only do the composite results document effective procedures to achieve high trans (anti) selectivities in intermolecular alkene cyclopropanation reactions but also relative reactivities indicate the extent to which regioselective cyclopropanation can be achieved. With 4-vinylcyclohexene, regioselectivities with the use of BDA can be predicted from Table IV, and additional examples are anticipated to show similar correspondence. Cyclopropane products derived from reactions with BDA are amenable to functionalization at the position α to the carbonyl group and can be employed for the synthesis of α-amino acids.[27]

Experimental Section

General Methods. NMR spectra were obtained on a Varian VXR-300 spectrometer; chemical shifts are reported in δ units with tetramethylsilane as the internal standard. Infrared spectra were recorded on an IBM IR/32 FT spectrometer, and mass spectra were obtained with the Hewlett-Packard 5995C GC/MS system operated at 70 eV. Analytical gas chromatographic analyses were performed on a Hewlett-Packard 5890A capillary GC with use of either SP-2330 or methylsilicone columns or both. Elemental analyses were performed by Texas Analytical Laboratories, Inc. Rhodium(II) acetate was prepared from rhodium trichloride;[28] rhodium(II) butyrate, trifluoroacetate, and perfluorobutyrate were synthesized by acetate displacement from stock rhodium-(II) acetate in the refluxing carboxylic acid that contained the corresponding anhydride.[29] Rhodium(II) trifluoroacetamide was obtained by heating rhodium(II) acetate in a melt of trifluoroacetamide at 140–150 °C according to the procedure of Bear.[30] Rhodium(II) thioacetate was prepared and characterized according to the literature procedure.[31] Alkenes were commercially available and were purified by distillation prior to use. Methanesulfonyl azide was prepared from methanesulfonyl chloride and sodium azide.[32]

2,3,4-Trimethyl-3-pentyl Diazoacetate (ODA). A mixture of 2,3,4-trimethyl-3-pentanol (9.75 g, 75.5 mmol), prepared by methyllithium addition to 2,4-dimethyl-3-pentanone, and anhydrous sodium acetate (0.043 g, 0.52 mmol) was heated to 90 °C in a 100-mL round-bottom flask fitted with an addition funnel containing diketene (6.98 g, 83.1 mmol). Addition of diketene to the rapidly stirred alcohol was allowed to occur dropwise over 20 min, and the resulting mixture was maintained at 90 °C for an additional 1 h. Distillation of the resulting acetoacetic ester (bp 42–44 °C at 0.05 Torr) yielded 9.45 g of a colorless liquid (44.7 mmol, 58% yield). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 4.93 (s, enol CH, 5%), 3.38 (s, keto CH$_2$, 95%), 2.67 (s, enol CH$_3$), 2.27 (s, keto CH$_3$), 2.26 (hept, J = 7.0 Hz, 2 H), 1.43 (s, ester CH$_3$ of keto form), 1.41 (s, ester CH$_3$ of enol form), 0.95 (d, J = 7.0 Hz, 6 H of keto form), 0.93 (d, J = 4.0 Hz, 6 H of keto form), and 0.92 and 0.88 (2 d, J = 7.0 Hz, 12 H of enol form).

2,3,4-Trimethyl-3-pentyl 3-oxobutanoate (6.40 g 30.3 mmol) was dissolved in 50 mL of anhydrous acetonitrile containing triethylamine (3.64 g, 36.0 mmol), and a solution of methanesulfonyl azide (4.48 g, 37.0 mmol) in 40 mL of acetonitrile was added dropwise to the stirred solution over 20 min. The resulting yellow solution of the diazoacetoacetate was maintained at room temperature for 4 h, and then 50 mL of 8% aqueous potassium hydroxide was added to effect acetyl cleavage. After being stirred for 24 h at room temperature, the solution was diluted by addition of water, the aqueous acetonitrile solution was washed with three 50-mL portions of ether, and the combined ether solution was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. ODA was purified by vacuum distillation (bp 84–87 °C at 0.1 Torr) to yield 3.46 g (17.4 mmol, 60% yield) of a brilliant yellow liquid. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 4.61 (s, CHN$_2$), 2.28 (hept, J = 6.9 Hz, 2 H), 1.43 (s, 3 H), 0.96 (d, J = 6.9 Hz, 6 H), and 0.94 (d, J = 6.9 Hz, 6 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 160.5, 94.2, 92.0, 46.5, 34.7, 28.1, 18.2, and 17.9. IR (neat): 2106 (C=N$_2$) and 1694 (C=O) cm^{-1}. Anal. Calcd for C$_{10}$H$_{18}$N$_2$O$_2$: C, 60.56; H, 9.17; N, 14.13. Found: C, 60.61; H, 9.24; N, 13.94.

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2-Methyl-3-isopropyl-3-heptyl Diazoacetate (UDA). Diketene (9.28 g, 110 mmol) was added dropwise over 30 min to a rapidly stirred mixture of 2-methyl-3-isopropyl-3-heptanol (17.23 g, 100 mmol), prepared by n-butyllithium addition to 2,4-dimethyl-3-pentanone, and sodium acetate (0.043 g, 0.5 mmol) that was maintained at 105 °C in a 250-mL round-bottom flask. After being stirred for an additional 90 min, the resulting acetoacetic ester was distilled (bp 91–94 °C at 0.1 Torr) to yield 15.0 g of a colorless liquid (58.6 mmol, 59% yield). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 4.95 (s, enol CH, 8%), 3.41 (s, keto CH$_2$, 92%), 2.67 (s, enol CH$_3$), 2.39 (hept, J = 7.0 Hz, 2 H), 2.28 (s, 3 H), 1.99–1.91 (m, 2 H), 1.32–1.24 (m, 4 H), 1.00 (d, J = 7.0 Hz, 6 H), 0.97 (d, J = 7.0 Hz, 6 H), and 0.90 (t, J = 7.1 Hz, 3 H).

Diazo transfer from methanesulfonyl azide (9.68 g, 80.0 mmol) to 2-methyl-3-isopropyl-3-heptyl 3-oxobutanoate (17.92 g, 70.0 mmol) was effected with the use of triethylamine (8.08 g, 79.9 mmol) in anhydrous acetonitrile at 40 °C (12 h), and acetyl cleavage was performed by using 40 mL of 15% aqueous potassium hydroxide according to the procedure previously described for the preparation of ODA. After isolation, UDA was purified by column chromatography on neutral alumina with dichloromethane as the eluent to yield 13.52 g of a clear yellow liquid (56.7 mmol, 81% yield). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 4.62 (s, CHN$_2$), 2.41 (hept, J = 7.0 Hz, 2 H), 2.00–1.92 (m, 2 H), 1.36–1.24 (m, 4 H), 1.01 (d, J = 7.0 Hz, 6 H), 0.99 (d, J = 7.0 Hz, 6 H), and 0.91 (t, J = 7.0 Hz, 3 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 160.2, 93.2, 46.4, 34.4, 33.6, 26.9, 23.6, 19.0, 18.9, and 14.1. IR (neat): 2106 (C=N$_2$) and 1696 (C=O) cm^{-1}. Anal. Calcd for C$_{13}$H$_{24}$N$_2$O$_2$: C, 64.96; H, 10.06; N, 11.66. Found: C, 64.87; H, 10.13; N, 11.60.

2,6-Di-tert-butyl-4-methylphenyl Diazoacetate (BDA). Diketene (4.20 g, 50.0 mmol) in 5.0 mL of anhydrous acetonitrile was added dropwise over 30 min to a rapidly stirred solution of 2,6-di-tert-butyl-4-methylphenol (5.51 g, 25.0 mmol), sodium acetate (0.21 g, 2.6 mmol), and methanesulfonyl azide (3.94 g, 32.6 mmol) in 20 mL of refluxing acetonitrile contained in a 100-mL three-neck flask fitted with a reflux condenser and an addition funnel. After addition was complete, the resulting brown solution was cooled to room temperature and stirring was continued for 7 h. The diazoacetoacetate product was isolated by adding water and extracting with ether, washing the ether extract with a 15% aqueous potassium hydroxide solution, and then drying the extract over anhydrous magnesium sulfate. Evaporation of the ether left a brown oil that was subjected to acetyl cleavage. Alternatively, addition of 30 mL of 15% aqueous potassium hydroxide solution precipitated a yellow powder that was filtered, washed with water, and dried. The resulting light yellow solid was identified as 2,6-di-tert-butyl-4-methylphenyl diazoacetoacetate (6.30 g, 19.0 mmol, 76% yield; mp 129–131 °C). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.13 (s, 2 H), 2.51 (s, CH$_3$CO), 2.33 (s, 3 H), and 1.34 (s, 18 H). A trace amount of BHT (<5%) was contained in the crude product. Anal. Calcd for C$_{19}$H$_{26}$N$_2$O$_3$: C, 69.06; H, 7.93; N, 8.48. Found: C, 69.13; H, 7.89; N, 8.53.

Acetyl cleavage was performed with the addition of 50 mL of 5% aqueous potassium hydroxide to 4.00 g of 2,6-di-tert-butyl-4-methylphenyl diazoacetoacetate (12.1 mmol) in 50 mL of acetonitrile. The solution was stirred for 2 h at room temperature, during which time a yellow precipitate formed in the reaction flask; then 75 mL of ether was added, and the aqueous solution was separated and washed twice with 75-mL portions of ether. The combined ether solution was washed with saturated aqueous sodium chloride and dried over anhydrous magnesium sulfate, and the ether was removed under reduced pressure to reveal the yellow BDA (3.05 g, 10.5 mmol, 87% yield). Recrystallization from ether afforded pure BDA, mp 151–153 °C dec. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.11 (s, 2 H), 5.01 (s, CHN$_2$), 2.31 (s, 3 H), and 1.35 (s, 18 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 142.5, 134.8, 127.0, 35.3, 31.5, and 21.5. IR (KBr): 2116 (C=N$_2$) and 1708 (C=O) cm^{-1}. Anal. Calcd for C$_{17}$H$_{24}$N$_2$O$_2$: C, 70.80; H, 8.39; N, 9.71. Found: C, 70.87; H, 8.46; N, 9.66.

Preparation of Dirhodium(II) Tetrakis(acetamide). A mixture of rhodium(II) acetate (0.25 g, 0.57 mmol) and acetamide (5.0 g, 85 mmol) in 50 mL of anhydrous chlorobenzene was refluxed under nitrogen in a Soxhlet extraction apparatus. The thimble was charged with a 3:1 mixture of sodium carbonate and sand that had been dried at 110 °C for 3 h, and a new thimble containing the sodium carbonate–sand mixture was introduced every 24 h. After 9 days, as evidenced by HPLC analysis on a μBondapak-CN column, the dirhodium composite was >99% Rh$_2$-(acam)$_4$. Chlorobenzene was removed by distillation and acetamide was sublimed to yield a purple solid. After the purple solid was heated in 50 mL of refluxing chlorobenzene for 24 h, isolation of the product revealed 0.25 g (85% yield) of a blue solid, whose color indicated the absence of axially bound ligands. ^{1}H NMR (CD$_3$CN, 300 MHz): δ 2.20 (s). Anal. Calcd for Rh$_2$C$_8$H$_{16}$O$_4$N$_4$: C, 21.93; H, 3.68; N, 12.79. Found: C, 22.20; H, 3.53; N, 12.81.

High Trans (Anti) Stereoselectivity in Cyclopropanation

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Catalytic Cyclopropanation Reactions. The diazo compound (0.50 mmol) dissolved in 3.0 mL of anhydrous dichloromethane was added at a controlled rate over a 5-h period to a stirred mixture of the alkene (5.0 mmol) and the rhodium(II) catalyst (0.005 mmol) in 3.0 mL of dichloromethane. Reactions were performed at room temperature except when $Rh_2(acam)_4$, which was catalytically effective in refluxing dichloromethane, was employed. Although $Rh_2(OAc)_4$ and $Rh_2(acam)_4$ were initially insoluble, homogeneous solutions were obtained immediately after the initial addition of the diazo compound. Within 2 h after addition was complete, the reaction solution was passed through a short alumina column with dichloromethane as the eluent to remove the catalyst. Solvent and excess alkene were distilled under reduced pressure, and the residue was weighed to obtain the product yield. Chromatographic analyses were performed with the use of methyl silicone and SP-2330 capillary columns to obtain the purity of the products and determine stereoselectivities. Duplicate experiments were performed to confirm stereoselectivities. Cyclopropane ester products formed from reactions with ODA and UDA were transesterified by using BF_3–OEt_2 in ethanol, and the resulting products were compared with authentic samples obtained from reactions with EDA.[3] The trans (anti) cyclopropane products from reactions with BDA were characterized by spectral and elemental analyses. The minor isomer was identified from its mass spectral fragmentation pattern, which was nearly identical with that of the trans (anti) isomer, and, where feasible, from its ^{1}H NMR spectral absorptions. Cyclopropane products from reactions of BDA with styrene and 1-hexene were further characterized by their independent syntheses from the corresponding ethyl esters, obtained as isomeric mixtures by $Rh_2(OAc)_2$-catalyzed cyclopropanation with EDA, through base hydrolysis (KOH in aqueous THF) and esterification of the lithium salt of BHT with the cyclopropanecarboxylic acid chloride.

The distribution of byproducts from decomposition of BDA varied greatly with the catalyst employed for the cyclopropanation reaction. In $Rh_2(OAc)_4$-catalyzed reactions, azine formation was dominant. For example, azine constituted 97% of the combination of azine, maleate, and fumarate byproducts from reactions performed with 4-vinylcyclohexene, and azine was the only byproduct from the reaction of BDA with cyclohexene. In $Rh_2(acam)_4$-catalyzed reactions, fumarate and maleate products (F/M = 1.5) were dominant. For example, fumarate and maleate esters accounted for 73% of these byproducts from reactions performed with 4-vinylcyclohexene and for 71% of the byproducts from reactions performed with cyclohexene. Similar results were obtained from reactions with the other alkenes employed in this study.

2,6-Di-*tert*-butyl-4-methylphenyl *trans*-2-Ethoxycyclopropane-carboxylate (4a). This compound was purified by flash chromatography on neutral alumina (97% hexane, 3% dichloromethane) and isolated as a mixture of isomers in 72% yield from the reaction of ethyl vinyl ether with BDA catalyzed by $Rh_2(OAc)_4$. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.09 (s, 2 H), 3.75 (d of t, J = 5.8, 1.9 Hz, CHO), 3.67 and 3.66 (2 q, J = 7.0 Hz, CH_2O), 2.30 (s, CH_3), 2.06 (d of t, J = 7.5, 1.9 Hz, CHCOO), 1.43 (d of d, J = 7.5, 5.8 Hz, 2 H), 1.36 (s, *t*-Bu), 1.33 (s, *t*-Bu), and 1.25 (t, J = 7.0 Hz, CH_3). Mass spectrum, *m/e* (relative abundance): 332 (M⁺, 0.2), 247 (1), 220 (6), 205 (6), 112 (14), 86 (5), 85 (100), 57 (15), and 55 (7). Cis isomer, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.09 (s, 2 H), 3.75–3.65 (m, 1 H), 3.60 (q, J = 7.0 Hz, CH_2O), 2.30 (s, CH_3), 1.96 (d of t, J = 9.0, 6.4 Hz, CHCOO), 1.57 (q, J = 7.0 Hz, 1 H), 1.36 (s, *t*-Bu), 1.35 (s, *t*-Bu), 1.30–1.20 (m, 1 H), and 1.15 (t, J = 7.0 Hz, CH_3). Mass spectrum, *m/e* (relative abundance): 332 (M⁺, 0.1), 247 (1), 220 (4), 205 (5), 112 (17), 86 (4), 85 (100), 57 (24), and 55 (7). Anal. Calcd for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70. Found: C, 75.78; H, 9.75.

2,6-Di-*tert*-butyl-4-methylphenyl *trans*-2-(*n*-Butyl)cyclopropane-carboxylate (4b). This compound was purified by flash chromatography on neutral alumina (97% hexane, 3% dichloromethane) and isolated in 90% yield from the reaction of 1-hexene with BDA catalyzed by Rh_2-(acam)$_4$. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.09 (s, 2 H), 2.30 (s, CH_3), 1.67 (d of d of d, J = 8.2, 4.4, 4.2 Hz, 1 H), 1.55–1.15 (m, 5 H), 1.34 (s, *t*-Bu), 1.33 (s, *t*-Bu), 0.92 (t, J = 7.1 Hz, CH_3), and 0.93–0.87 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 174.6, 142.1, 134.2, 127.2, 126.9, 35.3, 33.0, 31.6, 31.5, 31.4, 23.9, 22.4, 21.5, 16.2, and 14.0. Mass spectrum, *m/e* (relative abundance): 344 (M⁺, 0.8), 220 (1), 161 (2), 126 (5), 125 (50), 97 (10), 57 (11), and 55 (100). Cis isomer, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.09 (s, 2 H), 2.27 (s, CH_3), 1.96 (d to t, J = 8.2, 5.3 Hz, 1 H), 1.70–1.58 (m, 4 H), 1.50–1.20 (m, 2 H), 1.43 (s, *t*-Bu), 0.97–0.88 (m, 1 H), and 0.87 (t, J = 7.0 Hz, CH_3). Mass spectrum, *m/e* (relative abundance): 344 (M⁺, 2), 220 (4), 161 (3), 126 (5), 125 (57), 97 (16), 57 (14), and 55 (100). Anal. Calcd for $C_{23}H_{36}O_2$: C, 80.18; H, 10.53. Found: C, 80.11; H, 10.58.

2,6-Di-*tert*-butyl-4-methylphenyl *trans*-2-Phenylcyclopropane-carboxylate (4c). This compound was purified by flash chromatography on neutral alumina (98% hexane, 2% dichloromethane) and isolated in

86% yield from the reaction of 1-styrene with BDA catalyzed by Rh_2-(acam)$_4$. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35–7.18 (m, 5 H, Ph), 7.11 (s, 2 H), 2.70 (d of d of d, J = 9.2, 6.6, 4.2 Hz, 1 H), 2.32 (s, CH_3), 2.17 (d of d of d, J = 8.3, 5.0, 4.2 Hz, 1 H), 1.74 (d of d of d, J = 9.2, 5.0, 4.6 Hz, 1 H), 1.52 (d of d of d, J = 8.3, 6.6, 4.6 Hz, 1 H), 1.36 (s, *t*-Bu), and 1.35 (s, *t*-Bu). Mass spectrum, *m/e* (relative abundance): 364 (M⁺, 0.02), 207 (3), 146 (11), 145 (100), 127 (27), 117 (21), 115 (15), 91 (15), 77 (3), and 57 (9). Anal. Calcd for $C_{25}H_{32}O_2$: C, 82.37; H, 8.85. Found: C, 82.31; H, 8.90.

2,6-Di-*tert*-butyl-4-methylphenyl *trans*-2-*tert*-Butylcyclopropane-carboxylate (4d). This compound was purified by flash chromatography on neutral alumina (97% hexane, 3% dichloromethane) and isolated in 88% yield from the reaction of 3,3-dimethyl-1-butene with BDA catalyzed by $Rh_2(acam)_4$. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.09 (s, 2 H), 2.30 (s, CH_3), 1.79 (d of d of d, J = 8.2, 4.6, 4.5 Hz, CHCOO), 1.53 (d of d of d, J = 9.4, 7.3, 4.5 Hz, 1 H), 1.34 (s, 18 H), 1.19 (d of d of d, J = 9.4, 4.6, 4.4 Hz, 1 H), 1.00 (d of d of d, J = 8.2, 7.3, 4.4 Hz, 1 H), and 0.93 (s, *t*-Bu). Mass spectrum, *m/e* (relative abundance): 344 (M⁺, 2), 205 (2), 161 (2), 125 (19), 97 (9), 83 (15), 69 (21), 57 (14), and 55 (100). Anal. Calcd for $C_{23}H_{36}O_2$: C, 80.18; H, 10.53. Found: C, 80.03; H, 10.50.

2,6-Di-*tert*-butyl-4-methylphenyl *anti*-6-Bicyclo[3.1.0]hexane-carboxylate (4e). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.10 (s, 2 H), 2.32 (s, CH_3), 2.04 (t, J = 3.9 Hz, CHCOO), 2.0–1.6 (m, 8 H), and 1.36 (s, *t*-Bu). Mass spectrum, *m/e* (relative abundance): 328 (M⁺, 1.0), 220 (1), 110 (8), 109 (100), 81 (26), 57 (9), 55 (7), and 53 (7).

2,6-Di-*tert*-butyl-4-methylphenyl 2-Cyclopentenylacetate (6). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.12 (s, 2 H), 5.80 (m, 2 H), 3.27–3.16 (m, 1 H), 2.73 (d of d, J = 17.4, 7.1 Hz, 1 H), 2.64 (d of d, J = 17.4, 7.6 Hz, 1 H), 2.4–2.2 (m, 1 H), 2.31 (s, CH_3), 2.1–1.6 (m, 3 H), and 1.34 (s, *t*-Bu). Mass spectrum, *m/e* (relative abundance): 328 (M⁺, 0.3), 221 (10), 220 (60), 205 (39), 109 (14), 105 (4), 81 (5), 67 (100), 57 (18), and 55 (6).

2,6-Di-*tert*-butyl-4-methylphenyl *anti*-7-Bicyclo[4.1.0]heptane-carboxylate (4f). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.10 (s, 2 H), 2.32 (s, CH_3), 2.05–1.90 (m, 4 H), 1.85–1.75 (m, 4 H), 1.69 (t, J = 4.0 Hz, 1 H), 1.40–1.20 (m, 2 H), and 1.35 (s, *t*-Bu). Mass spectrum, *m/e* (relative abundance): 342 (M⁺, 0.1), 221 (2), 206 (3), 124 (9), 123 (100), 95 (40), 81 (14), 79 (19), 67 (15), 57 (12), and 55 (38).

2,6-Di-*tert*-butyl-4-methylphenyl 2-Cyclohexenylacetate (5). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.10 (s, 2 H), 5.74 (d, J = 10.2 Hz, 1 H), 5.66 (d, J = 10.2 Hz, 1 H), 2.80–2.65 (m, 1 H), 2.65 (d of d, J = 17.5, 6.3 Hz, 1 H), 2.5m (d of d, J = 17.5, 8.0 Hz, 1 H), 2.31 (s, CH_3), 2.04–1.90 (m, 2 H), 1.80–1.40 (m, 4 H), and 1.32 (s, *t*-Bu). Mass spectrum, *m/e* (relative abundance): 342 (M⁺, 0.3), 221 (46), 206 (26), 123 (17), 95 (12), 81 (100), 79 (16), 67 (8), 57 (22), and 55 (10).

2,6-Di-*tert*-butyl-4-methylphenyl *anti*-*exo*-Tricyclo[3.2.1.0²,⁴]octane-carboxylate (4g). This compound was purified by flash chromatography on neutral alumina (97% hexane, 3% dichloromethane) and isolated in 70% yield from the reaction of bicyclo[2.2.1]hept-2-ene with BDA catalyzed by $Rh_2(OAc)_4$. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.08 (s, 2 H), 2.46 (br s, 2 H), 2.30 (s, CH_3), 1.83 (t, J = 2.4 Hz, 1 H), 1.54–1.46 (m, 4 H), 1.38–1.31 (m, 2 H), 1.33 (s, 18 H), 1.02 (d of t, J = 10.8, 1.9 Hz, 1 H), and 0.76 (d, J = 10.8 Hz, 1 H). Mass spectrum, *m/e* (relative abundance): 354 (M⁺, 1), 220 (2), 205 (6), 136 (10), 135 (100), 107 (17), 91 (11), 79 (66), 57 (22), and 55 (39). Anal. Calcd for $C_{24}H_{34}O_2$: C, 81.31; H, 9.67. Found: C, 81.37; H, 9.63.

2,6-Di-*tert*-butyl-4-methylphenyl *anti*-2-Oxobicyclo[4.1.0]heptane-7-carboxylate (4h). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.08 (s, 2 H), 4.07 (d of d, J = 7.0, 1.7 Hz, 1 H), 3.80–3.64 (m, 1 H), 3.46–3.34 (m, 1 H), 2.31 (s, CH_3), 2.07 (d of d, J = 5.7, 1.7 Hz, 1 H), 2.15–1.82 (m, 2 H), 1.63–1.53 (m, 2 H) 1.32 (s, *t*-Bu), and 1.44–1.28 (m, 1 H). Mass spectrum, *m/e* (relative abundance): 344 (M⁺, 0.2), 220 (7), 205 (7), 125 (76), 124 (42), 97 (30), 83 (100), 81 (15), 79 (21), 69 (13), 57 (25), and 55 (44).

2,6-Di-*tert*-butyl-4-methylphenyl *trans*-2,2,3-Trimethylcyclopropane-carboxylate (4i). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.10 (s, 2 H), 2.30 (s, CH_3), 1.74 (d, J = 8.5 Hz, 1 H), 1.35 (s, CH_3), 1.34 (s, *t*-Bu), 1.26–1.34 (m, 1 H), 1.32 (s, CH_3), and 1.23 (d, J = 6.5 Hz, CH_3). ^{13}C NMR ($CDCl_3$; 75 MHz): δ 164.0, 137.9, 134.4, 126.2, 119.0, 118.9, 35.3, 27.9, 27.4, 23.8, 21.6, 19.1, 13.6, and 5.9. Mass spectrum, *m/e* (relative abundance): 330 (M⁺, 0.2), 205 (2), 133 (2), 112 (14), 111 (100), 69 (10), 57 (18), and 55 (58).

2,6-Di-*tert*-butyl-4-methylphenyl *trans*-2-(2-Methyl-1-propenyl)-3,3-dimethylcyclopropanecarboxylate (4j). This compound was purified by flash chromatography on neutral alumina (97% hexane, 3% dichloromethane) and isolated in 80% yield from the reaction of 2,5-dimethyl-2,4-hexadiene with BDA catalyzed by $Rh_2(OAc)_4$. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.08 (s, 2 H), 5.37 (d, J = 8.8 Hz, 1 H), 2.2. (s, CH_3), 2.09 (t, J = 8.7 Hz, 1 H), 1.97 (d, J = 8.6 Hz, 1 H), 1.70 (s, CH_3), 1.68

(s, CH₃), 1.34 (s, *t*-Bu), 1.30 (s, CH₃), 1.29 (s, CH₃), and 1.28 (s, *t*-Bu). Mass spectrum, *m/e* (relative abundance: 370 (M⁺, 0.4), 220 (8), 205 (7), 152 (11), 151 (100), 123 (87), 109 (34), 95 (12), 93 (10), 91 (12), 81 (43), and 79 (12). Anal. Calcd for C₂₅H₃₈O₂: C, 81.03; H, 10.33. Found: C, 80.91; H, 10.31.

2,6-Di-*tert*-butyl-4-methylphenyl *trans*-2-(3-Cyclohexen-1-yl)cyclo-propanecarboxylate (10). Cyclopropane derivatives were formed in 94% and 92% yield, respectively, from reactions catalyzed by Rh₂(OAc)₄ and Rh₄(acam)₄. ¹H NMR (CDCl₃, 300 MHz): δ 7.09 (s, 2 H), 5.68 (s, 2 H), 2.30 (s, CH₃), 2.24–1.80 (m, 5 H), 1.76 (quin, *J* = 4.1 Hz, 1 H), 1.56–1.41 (m, 2 H), 1.35 (s, 9 H), 1.33 (s, 9 H), 1.37–1.22 (m, 1 H), 1.16–1.00 (m, 1 H), and 0.94 (d of d of d, *J* = 10.8, 8.3, 4.1 Hz, 1 H). Mass spectrum, *m/e* (relative abundance): 368 (M⁺, 2), 220 (2), 161 (5), 149 (86), 131 (65), 121 (49), 119 (14), 105 (15), 93 (50), 91 (28), 79 (79), 77 (15), 71 (12), 67 (38), 57 (36), and 55 (100).

Catalytic Decomposition of BDA in the Absence of Alkene. The reaction was performed in dichloromethane with rhodium(II) acetate catalysis as previously described, and three dimeric products were isolated by flash chromatography and characterized spectroscopically. Fumarate ester (74%), ¹H NMR (CDCl₃, 300 MHz): δ 7.15 (s, 4 H), 7.10 (s, 2 H), 2.34 (s, 6 H), and 1.34 (s, 36 H). Mass spectrum, *m/e* (relative abundance): 520 (M⁺, 2), 220 (42), 217 (23), 205 (19), 203 (29), 82 (12), 57 (100). Maleate ester (13%), ¹H NMR (CDCl₃, 300 MHz): δ 7.28 (s, 4 H), 6.63 (s, 2 H), 2.29 (s, 6 H), and 1.33 (s, 36 H). Azine (13%), ¹H NMR (CDCl₃, 300 MHz): δ 7.16 (s, 4 H), 4.62 (s, 2 H), 2.32 (s, 6 H), and 1.34 (s, 36 H).

Reduction of BHT Cyclopropane Esters. 2,6-Di-*tert*-4-methylphenyl cyclopropanecarboxylate (1.5 mmol) in 10 mL of anhydrous ether was added dropwise over a 15-min period to a suspension of LiAlH₄ (6.0 mmol) in 30 mL of refluxing ether. The mixture was refluxed for an additional 24–48 h and then quenched with ethyl acetate, and the products were isolated after acidification and extraction. With the 2-*n*-butylcyclopropanecarboxylate (trans/cis = 2.0), the product mixture contained 67% *trans*-2-(*n*-butyl)cyclopropanemethanol, 7% *cis*-2-(*n*-bu-

tyl)cyclopropanemethanol, and 26% 2,6-di-*tert*-butyl-4-methylphenyl *cis*-2-(*n*-butyl)cyclopropanecarboxylate after a reaction time of 34 h. Similar results were obtained with the 2-phenylcyclopropanecarboxylate esters. In contrast, both cis and trans isomers of 2,6-di-*tert*-butyl-4-methylphenyl 2-ethoxycyclopropanecarboxylate were reduced by LiAlH₄ after 24 h in refluxing ether, and no isomerization of reactants or products was evident. Reductions of BHT cyclopropane esters formed from 1-hexene and styrene were virtually complete after 72 h (1-hexene, <5% cis BHT ester) adn 15 h (styrene) in refluxing THF. However, neither the trans nor the cis isomer of the BHT chrysanthemate ester **4j** underwent reduction in refluxing THF.

Relative Reactivities of Alkenes in Cyclopropanation Reactions. The diazo compound, (0.50 mmol), either ODA or BDA, in 3.0 mL of anhydrous methylene chloride was added at a controlled rate over a 5-h period to a stirred mixture of two alkenes (minimum amount of each olefin: 5.0 mmol), which normally included 1-hexene, and either Rh₂(OAc)₂ or Rh₂(acam)₄ (0.005 mmol) in 3.0 mL of dichloromethane. Reactions catalyzed by Rh₂(OAc)₄ were performed at room temperature, and those catalyzed by Rh₂(acam)₄ were run in refluxing dichloromethane, both under nitrogen. Products were isolated as previously described, and relative reactivities were obtained from product ratios determined by GC and ¹H NMR analyses. Duplicate experiments were performed for each pair of alkenes, and cross-checks of relative reactivity values were obtained from experiments with different sets of alkenes. Typical values for Rh₂(OAc)₄-catalyzed reactions of BDA were ethyl vinyl ether/1-hexene, 13; styrene/1-hexene, 3.8; and ethyl vinyl ether/styrene, 3.4.

Effects of Hydrogen Bonding on the Low-Lying Electronic States of a Model Polyene Aldehyde

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Abstract: Absorption spectra of crotonaldehyde in several alcohols demonstrate linear relationships between the energies of the lowest lying ¹ππ* and ¹nπ* transitions and the solvent pK_a, with the ¹ππ*–¹nπ* energy difference decreasing from 14 800 to 8500 cm⁻¹ in changing from ethanol (pK_a = 16.0) to perfluoro-*tert*-butanol (pK_a = 5.2). These results indicate that the pK_{HB} for hydrogen-bond formation is proprotional to the pK_a of the alcohol solvent in both the ground and excited states. The ability of strong hydrogen bonders to differentially shift low lying ¹ππ* and ¹nπ* states in polyene aldehydes has been used to invert the ¹ππ*/¹nπ* ordering and induce fluorescence in 2,4,6,8-decatetraenal, a model compound which does not emit in hydrocarbon environments. Absorption, fluorescence, and fluorescence excitation spectra of decatetraenal have been obtained in several hydrogen-bonding solvents over a range of temperatures. The fluorescence intensities are strongly temperature dependent and can be fit to a simple model involving a low-temperature ($T \leq 77$ K) equilibrium between a nonemitting, hydrogen-bonded complex and a fluorescent species which is either protonated or strongly hydrogen bonded. The changes in the optical spectra with temperature and the pK_a of the hydrogen bonder lead to a model in which the allowed transition between the hydrogen-bonded ground ("1¹A$_g$") and excited ("1¹B$_u$") states is followed by relaxation into an excited ¹ππ* state that at low temperatures favors a strongly hydrogen bonded or protonated form. Protonated decatetraenal has ¹ππ* lower than ¹nπ*, thus accounting for the observed fluorescence. Molecular orbital calculations support this model and also indicate an inversion of the "1¹B$_u$" and "2¹A$_g$" energy levels upon protonation.

1. Introduction

Linear polyenes are employed as chromophores in several important photobiological processes. Vision, photosynthesis, and

photoperiodism all depend on the unique chemistries of polyene excited states, and the characterization of these states has been a subject of considerable interest.[1–3] In addition to their roles in natural processes, polyenes are of intrinsic interest as "one-dimensional" conjugated systems, and progress in understanding

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