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Effect of Rhodium Carbenoid Structure on Cyclopropanation Chemoselectivity

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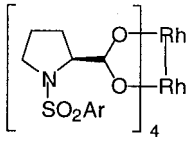
Abstract—Rhodium-stabilized carbenoids derived from aryldiazoacetates and vinyldiazoacetates undergo highly chemoselective intermolecular cyclopropanations, and this selectivity has been quantified by a Hammett study. These donor/acceptor substituted carbenoids are much more chemoselective than the traditional carbenoids derived from alkyl diazoacetates. © 2000 Published by Elsevier Science Ltd.

Introduction

The metal catalyzed decomposition of diazo compounds in the presence of alkenes is a powerful method for the construction of densely functionalized cyclopropanes. The most extensively utilized carbenoids (**1**) are those derived from diazoacetates.[1–4] Even though a wide range of alkenes can be used in this chemistry, in general, intermolecular cyclopropanations by these carbenoids are not particularly diastereoselective.[5,6] Furthermore, with most catalysts only moderate chemoselectivity occurs in competition reactions between different alkenes.[7] Highly asymmetric cyclopropanations, however, are possible with diazoacetates using a variety of chiral catalysts.[8–11]

1 **2**



Ar = *p*-($C_{11\text{-}13}H_{23\text{-}27}$)$C_6H_4$

3: Rh_2(*S*-DOSP)$_4$

Over the last 15 years we have explored the cyclopropanation chemistry of a different class of carbenoid (**2**), which is functionalized with both an electron withdrawing group and an electron-donating group (vinyl or aryl).[12,13] In contrast to the traditional diazoacetate system, cyclopropanations with vinyldiazoacetates and phenyldiazoacetates are routinely highly diastereoselective.[14–17] Furthermore, rhodium(II) prolinates such as Rh_2(*S*-DOSP)$_4$ (**3**) are exceptional chiral catalysts in vinyldiazoacetate and phenyldiazoacetate cyclopropanations,[15,17–20] even though these catalysts result in low enantioselectivity in ethyl diazoacetate cyclopropanations.[15]

During our extensive studies of aryl- and vinyldiazoacetates, it appeared to us that these carbenoids were much more chemoselective than those derived from diazoacetates. In this paper, we quantify the chemoselectivity differences between the various classes of carbenoids and demonstrate that vinyl and aryldiazoacetates are indeed considerably more chemoselective than unsubstituted diazoacetates. The first section will give a brief summary on the cyclopropanation chemistry of the traditional carbenoids derived from diazoacetates with emphasis on the chemoselectivity of this chemistry. This will be followed by a description of the cyclopropanation chemistry of carbenoids derived from vinyl- and phenyldiazoacetates, which will illustrate the synthetic utility of this chemistry and contrast the differences to diazoacetate cyclopropanations. In the results section a systematic study on the chemoselectivity of the various carbenoids will be described. Finally, the implications of these results on the future outlook of vinyl- and aryldiazoacetate chemistry will be considered.

Background on Diazoacetate Cyclopropanations

The decomposition of alkyl diazoacetates in the presence of alkenes is an excellent method for the synthesis of cyclopropanes.[1–4] The reaction is extremely general, with

Keywords: cyclopropanation; carbenes and carbenoids; diazo compounds; rhodium catalysis.

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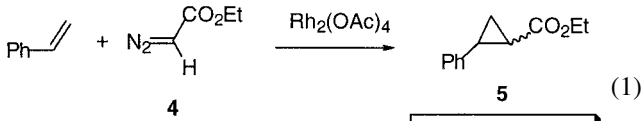
Table 1. Relative rates of cyclopropanation of various alkenes by ethyl diazoacetate

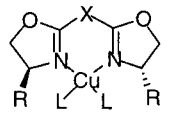
Alkene	$Rh_2(OAc)_4$	$Rh_2(acetamide)_4$
1-Hexene	1.0	1.0
Styrene	3.5	10
n-Butyl vinyl ether	8.6	15
Vinyl acetate	1.1	–
Cyclohexene	2.5	1.0
2,5-Dimethyl-2,4-hexadiene	2.1	2.0
2-Methyl-2-butene	1.5	–

electron rich, electron neutral, and even slightly electron deficient alkenes subject to cyclopropanation. A range of substitution patterns, from monosubstituted to tetrasubstituted can be tolerated. The major limitation of cyclopropanations by diazoacetates is that, in general, the cyclopropanations are not particularly stereoselective.[3,5] In the standard reaction of styrene with ethyl diazoacetate (**4**) catalyzed by dirhodium tetraacetate the diastereoselectivity is less than 2:1 favoring the *trans* isomer of cyclopropane **5** (Eq. (1)), although considerable enhancement in the diastereoselectivity can be achieved by using bulky ester derivatives.[6] The majority of catalysts have only a moderate effect on the diastereoselectivity of diazoacetate cyclopropanations but there are some notable exceptions.[1,2,21] Certain rhodium amide[6] and ruthenium[22–24] catalysts favor the formation of *trans* cyclopropanes while very bulky catalysts[25–28] can lead to a slight preference of *cis* cyclopropanes. Over a hundred types of chiral catalysts have been developed for asymmetric cyclopropanations by diazoacetates, and asymmetric induction of greater than 90% ee can be achieved with many of these catalysts.[8,9,11] The most notable are the copper catalysts **6**[29,30] and **7**,[31–33] the ruthenium catalysts **8**,[22–24] and the C_2-symmetric rhodium amide catalysts **9**[34] all of which contain chiral C_2-symmetric ligands. Rhodium(II) carboxylates have been generally ineffective at asymmetric cyclopropanations with diazoacetates.[35,36] A recent exception has been the biphenylcarboxylate derivative **10** that resulted in intermolecular cyclopropanation in high enantioselectivity.[37]



4 **5** (1)

E/*Z* ratio 1.8 : 1



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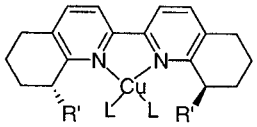

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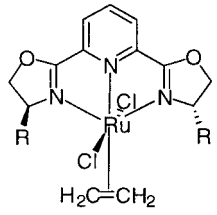

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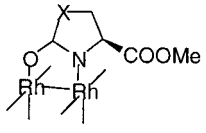

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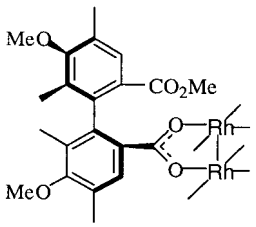
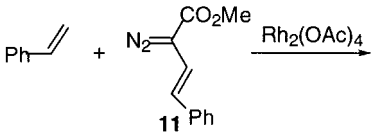


10

Several studies have been carried out to explore the relative reactivity of different alkenes towards cyclopropanation by diazoacetates,[1–4] and some selective examples are shown in Table 1.[5–7] The most commonly used catalyst for the decomposition of diazo compounds is dirhodium tetraacetate. With this catalyst the chemoselectivity is moderate, with only a 3.5 fold difference between 1-hexene and styrene. Slightly improved chemoselectivity was observed when dirhodium tetraacetamide was used as catalyst.[6] The most impressive chemoselectivity to date has been observed with an iron porphyrin catalyst, which resulted in a 74 fold difference between 1-decene and styrene.[38] This porphyrin catalyst, however, has not been broadly used in metal catalyzed transformations of diazo compounds.

Background on Vinyldiazoacetate and Phenyldiazoacetate Cyclopropanations

In recent years, it has become clear that carbenoids derived from vinyldiazoacetates have a very different reactivity profile to carbenoids derived from diazoacetates. Intermolecular cyclopropanations will only occur with monosubstituted alkenes, 1,1-disubstituted alkenes, and *cis* 1,2-disubstituted alkenes.[18] Furthermore, many of these reactions are highly diastereoselective as shown in Eq. (2) for the reaction of **11** with styrene,[14,18] again differing from the typical results obtained with the diazoacetate system. The highest diastereoselectivity is obtained with electron rich alkenes, such as styrene and vinyl ethers, and with vinylcarbenoids lacking an electron-withdrawing group on the vinyl portion. In many of the ideal systems, the second diastereomer cannot be observed in the NMR of the crude reaction mixtures. Similar highly diastereoselective cyclopropanations have been reported for the phenyldiazoacetate system **13** (Eq. (3)).[15–17] A comparison study of a range of carbenoid systems concludes that these highly diastereoselective cyclopropanations occur only in the case of carbenoids that are flanked with both an electron withdrawing group and an electron releasing group such as vinyl or phenyl.[15]



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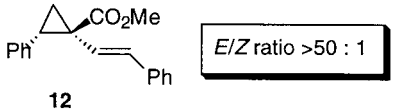

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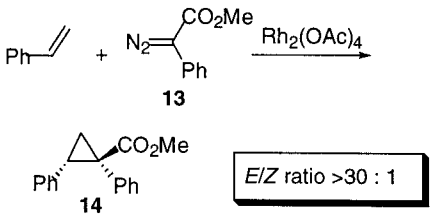
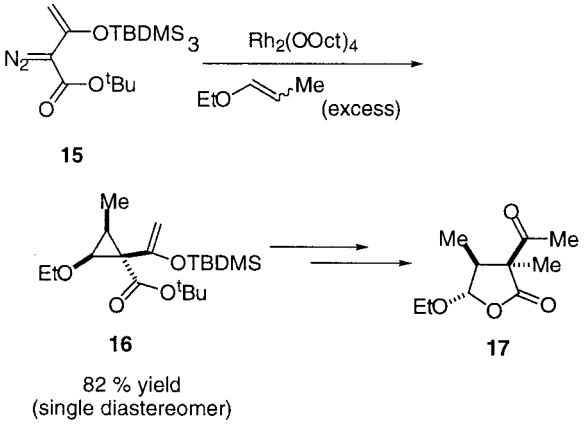


(3)

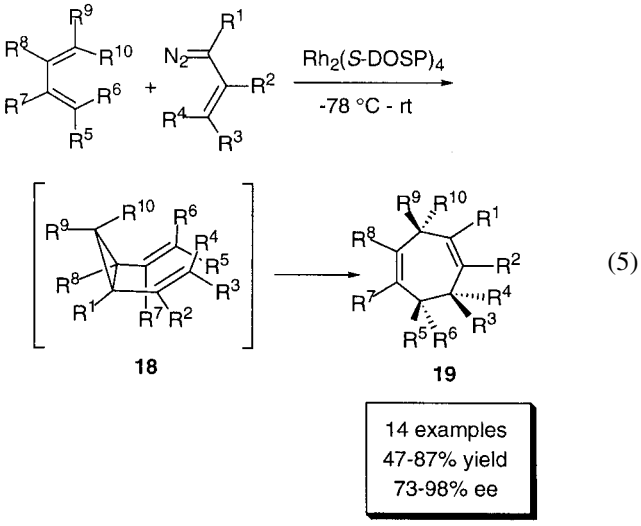
Rhodium(II) prolinates are extremely effective for asymmetric cyclopropanations with vinyldiazoacetates and phenyldiazoacetates even though they are poor chiral catalysts for diazoacetate cyclopropanations.[20,39] The highest asymmetric inductions are obtained when the reaction is carried out in non-polar solvents at low temperatures. Consequently, the most effective catalyst to date is Rh_2(*S*-DOSP)$_4$ (**3**), which is soluble in pentane even at −78°C. Rh_2(*S*-DOSP)$_4$ catalyzed decomposition of the vinyldiazoacetate **11** in the presence of styrene at −78°C results in cyclopropane **12** in 98% ee.[18]

Spectacular chemoselectivity and diastereoselectivity in this chemistry has been demonstrated on numerous occasions.[12,13] The key cyclopropanation step that was used in the synthesis of the ether analog of acetomycin **17** is a good illustrative example (Eq. (4)).[40] Decomposition of the vinyldiazoacetate **15** in the presence of an *E*/*Z* mixture of ethyl 1-propenyl ether results in the formation of **16**, containing three stereogenic centers, as a single diastereomer. Only the *Z* vinyl ether is capable of reacting with the carbenoid, and the high diastereoselectivity is typical of the vinyldiazoacetate system.



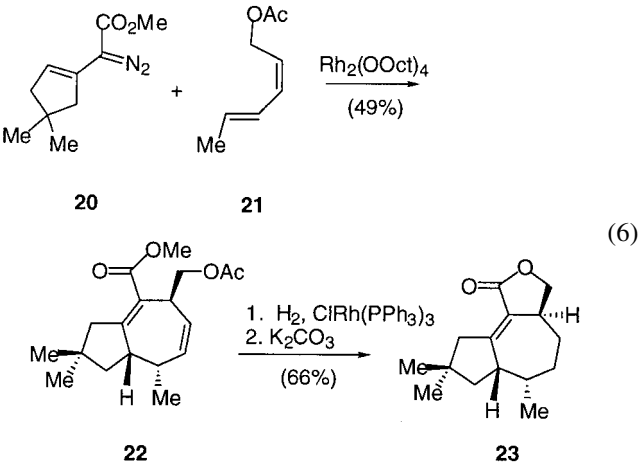
(4)

Vinyldiazoacetate cyclopropanations can be effectively used for the stereoselective synthesis of various ring systems because the resulting vinylcyclopropanes are prone to ring expansion in a stereoselective manner. The most exciting application of this chemistry is the formal [3+4] cycloadditions between vinyldiazoacetates and dienes.[12,41] The initially formed *cis*-divinylcyclopropanes **18** undergo a Cope rearrangement through a boat transition state to form cycloheptadienes with full control of relative stereochemistry at three stereogenic centers. Combined with the use of chiral catalyst **3**, this reaction results in the asymmetric synthesis of highly functionalized cycloheptadienes **19** (Eq. (5)).[42] The reaction is of very broad scope as a wide variety of dienes, including pyrroles, furans and benzenes can be used.



(5)

During the course of the cyclopropanation studies of vinyldiazoacetates and phenyldiazoacetates we became aware that there was a qualitative difference in the chemoselectivity of these carbenoids compared to the carbenoids derived from diazoacetates. This was readily seen in the reaction of vinyldiazoacetates with dienes.[12,41] In most instances, a single regioisomer of the cycloheptadienes (**19**) was formed which would mean that the initial cyclopropanation was highly regioselective. In contrast, the cyclopropanation reactions of ethyl diazoacetates with dienes often gave a mixture of regioisomers even when the diene was electronically biased to favor formation of one of the possible cyclopropanes.[43] A good example of the vinylcarbenoid regioselectivity is the key step in the synthesis of tremulenolide (**23**) in which the reaction of vinyldiazoacetate **20** with *E*,*Z* diene **21** gave a single cycloheptadiene derivative **22** that is formed by initial cyclopropanation of the *cis* double bond in **21**.[44]



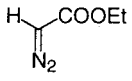
(6)

In this paper we describe a study to quantify the chemoselectivity of the rhodium-carbenoids derived from vinyl- and phenyldiazoacetates and unsubstituted diazoacetates.

The results confirm that the carbenoids derived from aryl- and vinyldiazoacetates are much more chemoselective than the traditional carbenoids derived from diazoacetates.

Results

At the onset of this study, a hypothesis was made that the combination of an electron withdrawing and electron donating group on the carbenoid considerably enhances the chemoselectivity of carbenoid cyclopropanations. We had seen some dramatic examples of how these types of carbenoids are sensitive to the steric environment of the trapping agent. We also suspected, however, that the carbenoid was sensitive to the electronic nature of that trapping agent. Consequently, reactions between a series of carbenoid systems and various monosubstituted alkenes were examined, as this would be a definitive test on how the carbenoid selectivity depends on carbenoid structure. Ethyl diazoacetate (**4**) was taken as the prototypical carbenoid precursor. This was then compared to the phenylvinyldiazoacetate **11**, which has been extensively used by us. In order to compare the effect of the electronic nature of the second group, diazoglutaconate **24**,[14] containing an electron withdrawing group on the vinyl group, and diazomalonate **25**[45] were examined. To complete the study two aryl diazoacetates **13** and **26**[46] were explored. If the original hypothesis is correct, both of these substrates would be expected to be highly chemoselective, with the methoxy substituted derivative being the most chemoselective.



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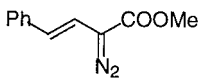

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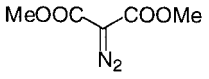

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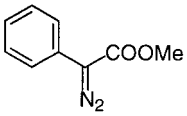

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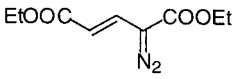

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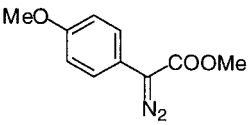
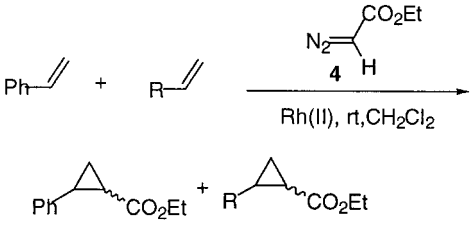


26

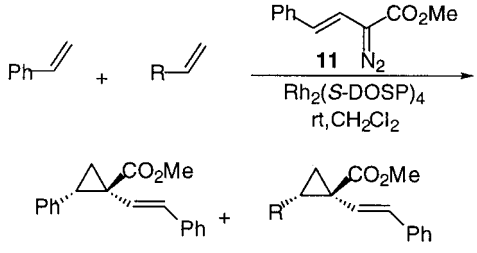
The first series of experiments was carried out to determine if there was any major difference between $Rh_2(S\text{-DOSP})_4$ and rhodium(II) acetate in controlling the chemoselectivity of cyclopropanations by ethyl diazoacetate (Eq. (7)). Each substrate was compared to styrene. The reactivity trends for cyclopropanations of ethyl diazoacetate catalyzed by $Rh_2(S\text{-DOSP})_4$ were similar to the published results of rhodium(II) acetate catalyzed reactions,[7] although the chemoselectivity was less pronounced in the $Rh_2(S\text{-DOSP})_4$ catalyzed reactions. Very little difference in reactivity was seen for the series of styrene derivatives consistent with virtually no build-up of positive charge at the benzylic carbon in the transition state of these diazoacetate cyclopropanations.



(7)

	Relative rate versus styrene	
R	$Rh_2(S\text{-DOSP})_4$	$Rh_2(OAc)_4$
p-$MeOC_6H_4$	0.90	0.90
p-$CH_3C_6H_4$	1.0	
p-ClC_6H_4	1.0	
p-$CF_3C_6H_4$	0.70	
n-Bu	0.31	0.29[3]
n-BuO	1.3	2.5[3]

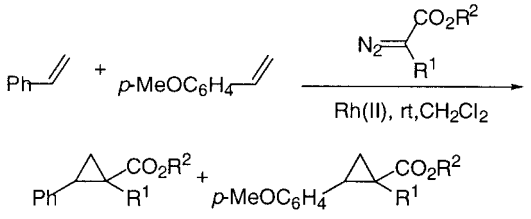
The next series of experiments was carried out with vinyldiazoacetate **11** so that the influence of the electron donating phenylvinyl functionality on the chemoselectivity could be determined. These reactions were carried out in CH_2Cl_2 at room temperature using $Rh_2(S\text{-DOSP})_4$ as catalyst. In contrast to the ethyl diazoacetate cyclopropanations, the reactions with vinyldiazoacetate **11** were highly chemoselective (Eq. (8)). The selectivity between styrene and 1-hexene was around 50, compared to 3.3 for the ethyl diazoacetate system. Considerable differences in the relative rate of reaction of **11** with the various substituted styrenes were also observed. The Hammett analysis of the reactions of **11** is shown in Fig. 1. A much closer fit was observed for the graph in which the relative reactivity was plotted against $\sigma+$ (R=0.99) rather than σ (R=0.83). This result indicates that charge build up at the benzylic position does occur for cyclopropanations of styrenes with **11**. Even though the ρ value of -1.0 indicates that the extent of the charge build up is only moderate, resonance effects stabilize this charge build-up.



(8)

	Relative rate versus styrene
R	$Rh_2(S\text{-DOSP})_4$
p-$MeOC_6H_4$	8.3
p-$CH_3C_6H_4$	3.9
p-ClC_6H_4	1.3
p-$CF_3C_6H_4$	0.39
n-Bu	0.02
n-BuO	4.0

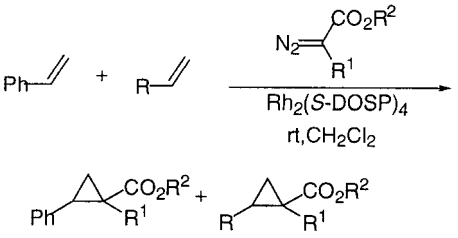
The effect of solvent and catalyst was then further explored by comparing the selectivity of reactions between ethyl diazoacetate (**4**) and the vinyldiazoacetate **11** with styrene and 4-methoxystyrene (Eq. (9)). In the case of ethyl diazoacetate, virtually no chemoselectivity between styrene and 4-methoxystyrene was observed under all the reaction conditions that were examined. With vinyldiazoacetate **11**, the chemoselectivity was considerably greater. The highest chemoselectivity was obtained when electron deficient catalysts such as $Rh_2(S\text{-DOSP})_4$ or $Rh_2(TFA)_4$ were used. Even though solvent can play a critical role in the outcome of many vinylcarbenoid reactions,[47–49] the chemoselectivity was virtually independent of solvent.



(9)

Catalyst	Solvent	Relative rate versus styrene: Diazo **4**	Relative rate versus styrene: Diazo **11**
$Rh_2(OAc)_4$	CH_2Cl_2	0.90	5.2
$Rh_2(TFA)_4$	CH_2Cl_2	1.1	8.1
$Rh_2(S\text{-DOSP})_4$	CH_2Cl_2	0.90	8.3
$Rh_2(S\text{-DOSP})_4$	Hexane	0.80	8.1

In order to further test the hypothesis that an electron-donating group was required on the diazoacetate in order to have high chemoselectivity, the next series of experiments were carried out on diazoglutaconate **24** and diazomalonate **25** (Eq. (10)). Diazoglutaconate **24** displays many of the characteristics of vinyldiazoacetate **11** but the resulting carbenoid behaves as an extremely electrophilic species that will even cyclopropanate benzene.[50] The carbenoid derived from diazomalonate is also very reactive as it is functionalized by two electron-withdrawing groups. Remarkably, even though both systems might be expected to generate a more reactive carbenoid than that derived from ethyl diazoacetate, both are considerably more chemoselective in the competition reactions than the diazoacetate carbenoid. However, neither is as selective as the vinyldiazoacetate **11**. In the Hammett studies, the best correlation was found when the rate selectivity was plotted against $\sigma+$. With the diazoglutaconate **24**, ρ was -0.7, while with diazomalonate **25**, ρ was -0.2. Thus, cyclopropanation with a carbenoid from a diazoacetate with a vinylogous ester as the second functionality (**24**) results in considerably greater charge build-up in the transition-state than that of a carbenoid derived from diazomalonate (**25**).



(10)

R	Relative rate versus styrene: **24** (EtOOC, COOEt, N_2)	Relative rate versus styrene: **25** (MeOOC, COOMe, N_2)
p-$MeOC_6H_4$	3.4	1.5
p-$CH_3C_6H_4$	1.5	0.85
p-ClC_6H_4	1.1	1.1
p-$CF_3C_6H_4$	0.38	0.65
n-Bu	0.03	0.08

The final series of experiments were carried out on the aryldiazoacetates **13** and **26**. On the basis of the original hypothesis the presence of the aryl group would be expected to lead to a carbenoid that would be highly chemoselective. This proved to be the case as shown in the competition studies summarized in Eq. (11). In the competition studies between styrene and 1-hexene only a trace of the product derived from cyclopropanation of 1-hexene was observed. In the Hammett study ($\sigma+$) with a series of styrenes, ρ of -1.0 was obtained for the phenyldiazoacetate **13**, while ρ of -1.3 was obtained for the 4-methoxyphenyldiazoacetate **26**. Once again, the highest chemoselectivity was observed for the diazoacetate functionalized with the most electron-donating group.

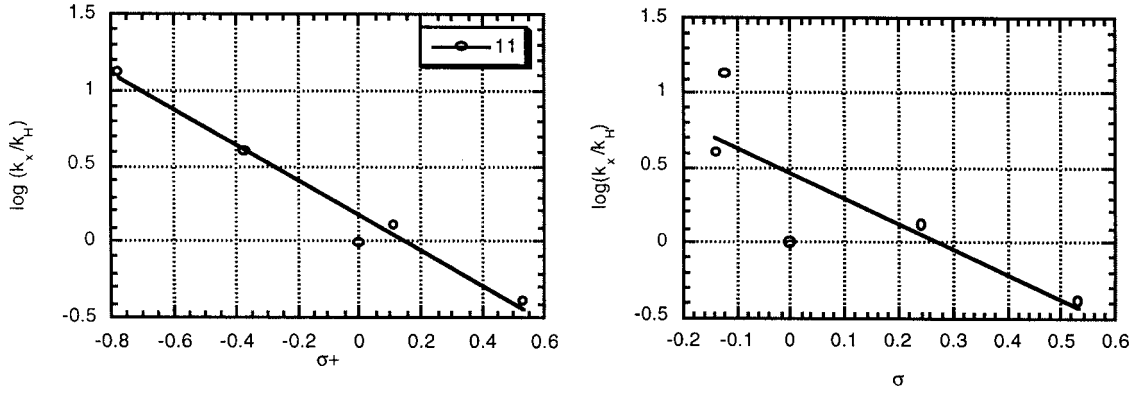
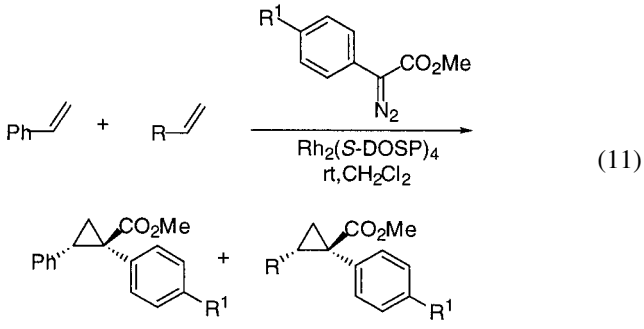


Figure 1. Hammet plot of relative rates of cyclopropanation by **11**.



(11)

R	Relative rate versus styrene	
	Diazo **13** R^1=H	Diazo **26** R^1=OMe
p-$MeOC_6H_4$	8.4	18
p-$CH_3C_6H_4$	1.9	3.2
p-ClC_6H_4	1.1	1.3
p-$CF_3C_6H_4$	0.43	0.40
n-Bu	0.02	0.03
n-BuO	5.7	

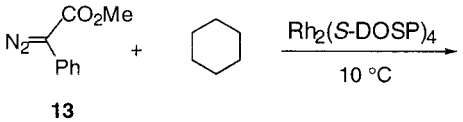
The Hammett studies demonstrate that the structure of the carbenoid has a major effect on the chemoselectivity of the cyclopropanation, and that this effect dominates over rhodium catalyst structure and solvent used. The least selective carbenoid was that derived from ethyl diazoacetate. Even carbenoids derived from diazoglutaconate or diazomalonate are more selective than diazoacetate. Functionalization of the diazoacetate with an electron-donating group results in a much more chemoselective carbenoid. Presumably, the electron donating group would stabilize the highly electron deficient carbenoid. Consequently, cyclopropanation with this carbenoid proceeds through a later transition state than the carbenoid derived from diazoacetate, and during the formation of a late transition state, there is more opportunity for charge build up to occur.

Future Outlook for Vinyldiazoacetate and Aryldiazoacetate Chemistry

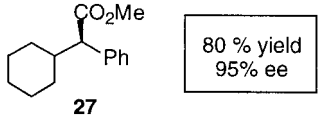
The observation that the carbenoids derived from vinyldiazoacetates and phenyldiazoacetates are much more stabilized and chemoselective than the traditional carbenoids derived from diazoacetates offers exciting new opportunities for the utilization of metal-stabilized carbenoids in organic synthesis. One of the most challenging problems in diazoacetate cyclopropanations is the control of diastereoselectivity, while with the donor/acceptor-substituted carbenoids, high diastereoselectivity is the routine outcome.[12,13] Similarly, Rh_2(*S*-DOSP)$_4$, which is ineffective at asymmetric diazoacetate cyclopropanations, is exceptional for cyclopropanations by donor/acceptor substituted carbenoids.[20] Both of these effects have been proposed to be caused by the more demanding requirement for the trajectory of approach of the alkene to the donor/acceptor-substituted carbenoids compared to the carbenoid derived from diazoacetate.[20] A more demanding approach would be consistent with a reaction that proceeds through a later transition state.

An even more interesting possibility would be that the added stability of the donor/acceptor-substituted carbenoids could enable transformations to be achieved that simply were not feasible with carbenoids derived from diazoacetates. An especially promising development is the discovery that aryldiazoacetates are capable of very effective asymmetric intermolecular C–H insertions.[51] In the case of diazoacetates, only the intramolecular C–H insertions are considered to be synthetically viable. The carbenoids derived from diazoacetates are poorly selective in intermolecular C–H insertions, and are prone to dimerization.[3,4,52]

Due to the added stabilization of the aryldiazoacetate carbenoids dimerization of the carbenoid is considerably less prevalent such that effective C–H insertions into alkanes can be achieved.[53] An illustrative example is the reaction of methyl phenyldiazoacetate with cyclohexane catalyzed by Rh_2(*S*-DOSP)$_4$ at 10°C, which results in the formation of **27** in 95% ee (Eq. (12)).[54] Selectivity is also possible between different C–H bonds as seen in the reaction with 2-methybutane where clean insertion into the tertiary C–H bond is observed to form **28** (Eq. (13)).[54] This result should be contrasted with the reaction of ethyl diazoacetate and 2-methylbutane, where C–H insertion at every possible position is observed.[55] Further demonstration of the synthetic utility of the intermolecular C–H insertion was recently described in a direct synthesis of ritalin in the reaction between phenyldiazoacetate and N-BOC-piperidine[56,57] and the asymmetric synthesis of syn-aldol products by the reaction between aryldiazoacetates and allyl silyl ethers.[58] A notable feature of the second transformation is that excellent control of diastereoselectvity is also possible in this chemistry.

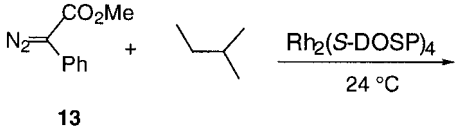


13

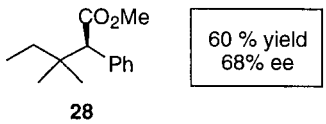


27

(12)



13



28

(13)

In summary, the reactions of rhodium-stabilized carbenoids derived from aryl- and vinyldiazoacetates display considerable versatility in organic synthesis. These donor/acceptor substituted carbenoids often undergo highly stereoselective transformations. In the study described herein, quantitative data has been obtained that demonstrates that these carbenoids are much more chemoselective than the traditional

carbenoid derived from ethyl diazoacetate. Presumably, these donor/acceptor substituted carbenoids are considerably more stabilized compared to the diazoacetate carbenoid, and this in turn, explains why they are capable of such selective transformations.

Experimental

Methyl 2-diazo-4-phenyl-3-butenoate (**11**),[18] diethyl 4-diazo-2-pentenedioate (**24**),[59] dimethyl diazomalonate (**25**),[59] methyl phenyldiazoacetate (**13**),[51] methyl 4-methoxyphenyldiazoacetate (**26**),[46] [dimethyl 2-phenylcyclopropane-1,1-dicarboxylate,[18] methyl 2β-butyl-1β-(2-(*E*)-styryl) cyclopropane-1α-carboxylate,[18] methyl 2β-(4-methoxyphenyl)-1β-(2-(*E*)-styryl)cyclopropane-1α-carboxylate,[18] methyl 2β-(4-chlorophenyl)-1β-(2-(*E*)-styryl)cyclopropane-1α-carboxylate,[18] were prepared by literature procedures.

General Procedure for Rhodium(II)-Catalyzed Decompositions of Diazomethanes in the Presence of Alkenes

A mixture of alkene (5.0 equiv.) and Rh(II) catalyst (0.01 equiv.) in solvent was stirred at room temperature under an argon atmosphere. To this solution was added the diazoacetate (1 equiv., 0.09 M) in solvent over 10 min, and the mixture was then stirred for 3–4 h. The mixture was then concentrated in vacuo, and the residue was purified on silica using petroleum ether/ether as the eluent in the ratio specified in parentheses.

Methyl 2β-(4-trifluoromethylphenyl)-1β-(2-(*E*)-styryl)-cyclopropane-1α-carboxylate. (9:1) 63% yield. IR (neat) 3031, 3295, 1730, 1327, 1119 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, 2H, J=8.5 Hz), 7.30–7.60 (m, 5H), 7.15 (d, 2H, J=8.5 Hz), 6.38 (d, 1H, J=16.0 Hz), 6.10 (d, 1H, J=16.0 Hz), 3.76 (s, 3H), 3.02 (dd, 1H, J=9.0, 5.0 Hz), 2.06 (dd, 1H, J=9.0, 5.0 Hz), 1.85 (dd, 1H, J=5.0, 2.0 Hz); ^{13}C NMR ($CDCl_3$) δ 173.6, 139.8 (q, J=1.4 Hz), 136.5, 133.8, 129.2, 128.8 (q, J=32.4 Hz), 128.4, 127.6, 126.2, 124.8 (q, J=4.1 Hz), 124.1 (q, J=270.1 Hz), 123.2, 52.5, 34.0, 33.7, 18.5. Anal. Calcd for $C_{20}H_{17}F_3O_2$: C, 69.36; H, 4.95. Found: C, 69.25; H, 4.99.

Methyl 2β-phenyl-1β-(2-(*E*)-styryl)cyclopropane-1a-carboxylate. (9:1) 98% yield. IR (neat) 3084, 3062, 3030, 2950, 1736, 1490, 1454, 1241, 1132, 969, 708; ^1H NMR (500 MHz, $CDCl_3$) δ 7.50–7.35 (m, 3H), 7.30–7.08 (m, 12H), 6.46 (d, 1H, J=27 Hz), 6.18 (d, 1H, J=27 Hz), 3.40 (s, 3H), 2.62 (d, 1H, J=9 Hz), 2.05 (d, 1H, J=9 Hz); ^{13}C NMR ($CDCl_3$) δ 171.2, 142.2, 140.8, 137.3, 130.9, 129.9, 128.8, 128.3, 128.3, 128.3, 127.2, 126.8, 126.8, 126.7, 126.1, 51.8, 47.1, 38.8, 22.5. HRMS (EI) calcd for $C_{25}H_{22}O_2$, 354.1620, found 354.1665.

Methyl 2β-(4-methylphenyl)-1β-(2-(*E*)-styryl)cyclopropane-1α-carboxylate. (9:1) 82% yield. Mp 64–66°C; IR (neat) 3089, 3031, 2956, 2924, 1721, 1438, 1252, 1151; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30–7.10 (m, 5H), 7.01 (s, 4H), 6.35 (d, 1H, J=16.2 Hz), 6.15 (d, 1H, J=16.2 Hz), 3.74 (s, 3H), 2.96 (dd, 1H, J=9.2, 7.6 Hz), 2.25 (s, 3H), 2.00 (dd, 1H, J=9.2, 4.8 Hz), 1.78 (dd, 1H, J=7.6, 4.8 Hz); ^{13}C NMR ($CDCl_3$) δ 174.2, 137.1, 136.3, 132.9, 132.3, 128.9, 128.7, 128.3, 127.3, 126.2, 124.2, 52.3, 34.8, 33.2, 20.9, 18.6. Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.22; H, 7.01.

Methyl 2β-butoxy-1β-(2-(*E*)-styryl)cyclopropane-1α-carboxylate. (9:1) 60% yield. IR (neat) 2962, 2930, 2871, 1721 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, 2H, J=7.0 Hz), 7.30 (t, 2H, J=7.5 Hz),7.20(t, 1H, J=7.5 Hz), 6.74 (d, 1H, J=16.0 Hz), 6.42 (d, 1H, J=16.0 Hz), 3.77 (m, 1H), 3.73 (s, 3H), 3.47 (dt, 1H, J=6.5, 6.0 Hz), 3.33 (dt, 1H, J=7.0, 6.5 Hz), 1.87 (t, 1H, J=7.0 Hz), 1.64 (t, 1H, J=6.0 Hz), 1.43 (m, 2H), 1.26 (m, 2H), 0.79 (t, 3H, J=7.5 Hz); $^{13}CNMR$ ($CDCl_3$) δ 172.9, 137.5, 129.7, 128.4, 127.0, 126.1, 121.5, 71.6, 68.2, 52.1, 31.7, 31.4, 21.6, 19.2, 13.7. Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.56; H, 8.05.

Ethyl 2β-butyl-1β-((*E*)-2-ethoxycarbonylvinyl)cyclopropane-1α-carboxylate. (3:1) 68% yield. IR (neat) 2990, 2963, 2936, 2865, 2869, 1729, 1654, 1273, 1181, 1037 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.31 (d, 1H, J=16.0 Hz), 5.70 (d, 1H, J=16.0 Hz), 4.12 (dq, 4H, J=7.1, 3.8 Hz), 1.77–1.70 (m, 1H), 1.63 (dd, 1H, J=4.7, 4.4 Hz), 1.40–1.10 (m, 12H), 1.00 (dd, 1H, J=7.1, 4.4 Hz), 0.90–0.70 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 172.7, 166.3, 143.6, 121.2, 61.1, 60.2, 33.8, 31.3, 30.0, 27.3, 22.1, 21.1, 14.1, 14.0, 13.8. Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01. Found: C, 66.88; H, 8.98.

Ethyl 1β-((*E*)-2-ethoxycarbonylvinyl)-2β-(4-trifluoromethylphenyl)cyclopropane-1α-carboxylate. (4:1) 81% yield. IR (neat) 2990, 2946, 2908, 2882, 1730 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, 2H, J=8.5 Hz), 7.25 (d, 2H, J=8.0 Hz), 6.89 (d, 1H, J=16.0 Hz), 5.68 (d, 1H, J=16.0 Hz), 4.26 (q, 2H, J=7.0 Hz), 4.08 (q, 2H, J=7.0 Hz), 3.22 (dd, 1H, J=9.0, 7.5 Hz), 2.12 (dd, 1H, J=9.0, 5.5 Hz), 1.80 (dd, 1H, J=7.5, 5.5 Hz), 1.32 (t, 3H, J=7.0 Hz), 1.18 (t, 3H, J=7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 171.5, 165.7, 141.5, 138.7 (q, J=1.4 Hz), 129.7, 129.4 (q, J=32.3 Hz), 125.1 (q, J=4.1 Hz), 124.0 (q, J=270.5 Hz), 122.4, 61.7, 60.2, 36.3, 32.5, 19.7, 14.1, 14.0. Anal. Calcd for $C_{18}H_{19}F_3O_4$: C, 60.67; H, 5.37. Found: C, 60.71; H, 5.36.

Ethyl 1β-((*E*)-2-ethoxycarbonylvinyl)-2β-(4-chlorophenyl)-cyclopropane-1α-carboxylate. (4:1) 78% yield. IR (neat) 2990, 2935, 2903, 1721 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, 2H, J=9.0 Hz), 7.06 (d, 2H, J=9.0 Hz), 6.90 (d, 1H, J=16.0 Hz), 5.64 (d, 1H, J=16.0 Hz), 4.24 (q, 2H, J=7.0 Hz), 4.09 (q, 2H, J=7.0 Hz), 3.15 (dd, 1H, J=9.0, 7.5 Hz), 2.08 (dd, 1H, J=9.0, 5.5 Hz), 1.72 (dd, 1H, J=7.5, 5.5 Hz), 1.31 (t, 3H, J=7.0 Hz), 1.21 (t, 3H, J=7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 171.6, 165.8, 141.8, 133.0, 132.9, 130.6, 128.4, 121.9, 61.6, 60.2, 36.4, 32.3, 19.9, 14.1, 14.1. Anal. Calcd for $C_{17}H_{19}ClO_4$: C, 63.26; H, 5.93. Found: C, 63.19; H, 5.92.

Ethyl 1β-((*E*)-2-ethoxycarbonylvinyl)-2β-phenylcyclopropane-1α-carboxylate. (7:3) 95% yield. IR (neat) 1725, 1655 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.3–7.1 (m, 5H), 6.90 (d, 1H, J=15.9 Hz), 5.92 (d, 1H, J=15.9 Hz), 4.24 (q, 1H, J=7.1 Hz), 4.06 (q, 1H, J=7.1 Hz), 3.20 (dd,

1H, *J*=9.3, 8.0 Hz), 2.09 (dd, 1H, *J*=9.3, 5.1 Hz), 1.75 (dd, 1H, *J*=8.0, 5.1 Hz), 1.32 (t, 3H, *J*=7.1 Hz), 1.18 (t, 3H, *J*=7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 172.0, 166.0, 142.4, 134.4, 129.4, 128.3, 127.3, 121.7, 61.5, 60.1, 37.4, 32.3, 20.1, 14.2, 14.1. Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.80; H, 7.03.

Ethyl 1β-((*E*)-2-ethoxycarbonylvinyl)-2β-(4-methylphenyl)cyclopropane-1α-carboxylate. (4:1) 84% yield. IR (neat) 2983, 1726, 1252, 1183 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (d, 2H, *J*=7.8 Hz), 7.01 (d, 2H, *J*=8.4 Hz), 6.91 (d, 1H *J*=15.9 Hz), 5.66 (d, 1H, *J*=15.9 Hz), 4.23 (q, 2H, *J*=7.2 Hz), 4.07 (q, 2H, *J*=7.2 Hz), 3.17 (dd, 1H, *J*=9.0, 7.8 Hz), 2.29 (s, 3H), 2.07 (dd, 1H, *J*=9.0, 5.0 Hz), 1.73 (dd, 1H, *J*=7.8, 5.0 Hz), 1.31 (t, 3H, *J*=7.2 Hz), 1.19 (t, 3H, *J*=7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 172.0, 166.0, 142.5, 136.8, 131.2, 129.2, 128.9, 121.5, 61.3, 60.0, 37.3, 32.2, 20.9, 20.1, 14.1, 14.0. Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.44; H, 7.28.

Ethyl 1β-((*E*)-2-ethoxycarbonylvinyl)-2β-(4-methoxyphenyl)cyclopropane-1α-carboxylate. (7:3) 88% yield. IR (neat) 1725, 1655 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (d, 2H, *J*=8.6 Hz), 6.86 (d, 1H, *J*=15.9 Hz), 6.79 (d, 2H, *J*=8.6 Hz), 5.61 (d, 1H, *J*=15.9 Hz), 4.23 (q, 2H, *J*=7.0 Hz), 4.07 (q, 2H, *J*=7.1 Hz), 3.77 (s, 3H), 3.15 (dd, 1H, *J*=9.1, 7.6 Hz), 2.07 (dd, 1H, *J*=9.1, 5.0 Hz), 1.70 (dd, 1H, *J*=7.6, 5.0 Hz), 1.31 (t, 3H, *J*=7.1 Hz), 1.20 (t, 3H, *J*=73.1 Hz); ^{13}C NMR ($CDCl_3$) δ 172.0, 166.1, 158.7, 142.6, 130.5, 126.3, 121.4, 113.7, 61.5, 60.2, 55.2, 37.3, 20.5, 14.3, 14.2. Anal. Calcd for $C_{18}H_{22}O_4$: C, 67.91; H, 6.96. Found: C, 67.99; H, 7.01.

Dimethyl 2-butylcyclopropane-1,1-dicarboxylate. (3:1) 41% yield. IR (neat) 2956, 2930, 2871, 1742, 1438, 1332, 1284, 1215, 1135 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.72 (s, 3H), 3.68 (s, 3H), 1.87 (m), 1.50–1.21 (m, 7H), 1.20–1.07 (m, 1H), 0.84 (t, 3H, *J*=7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 170.9, 168.7, 52.5, 52.4, 33.9, 31.0, 28.8, 28.3, 22.3, 21.4, 13.9. Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.91; H, 8.46.

Dimethyl 2-(4-trifluoromethylphenyl)cyclopropane-1,1-dicarboxylate. (4:1) 56% yield. IR (neat) 3010, 2962, 1745, 1452 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, 2H, *J*=8.4 Hz), 7.32 (d, 2H, *J*=8.4 Hz), 3.80 (s, 3H), 3.39 (s, 3H), 3.26 (dd, 1H, *J*=9.6, 8.1 Hz), 2.22 (dd, 1H, *J*=8.1, 5.4 Hz), 1.79 (dd, 1H, *J*=9.6, 5.4 Hz); ^{13}C NMR ($CDCl_3$) δ 169.7, 166.6, 138.8, 129.5 (q, J=32.4 Hz), 128.7, 125.0 (q, J=3.6 Hz), 124.0 (q, J=270.1 Hz), 52.8, 52.3, 37.3, 31.7, 19.0. Anal. Calcd for $C_{14}H_{13}F_3O_4$: C, 55.63; H, 4.34. Found: C, 55.78; H, 4.47.

Dimethyl 2-(4-chlorophenyl)cyclopropane-1,1-dicarboxylate. (4:1) 65% yield. IR (neat) 3009, 2956, 2850, 1737 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, 2H, *J*=8.5 Hz), 7.13 (d, 2H, *J*=8.5 Hz), 3.79 (s, 3H), 3.40 (s, 3H), 3.18 (dd, 1H, *J*=9.0, 8.0 Hz), 2.15 (dd, 1H, *J*=8.0, 5.0 Hz), 1.74 (dd, 1H, *J*=9.0, 5.0 Hz); ^{13}C NMR ($CDCl_3$) δ 169.8, 166.7, 133.2, 133.0, 129.7, 128.2, 52.8, 52.3, 37.1, 31.6, 19.0. Anal. Calcd for $C_{13}H_{13}ClO_4$: C, 58.11; H, 4.88. Found: C, 58.40; H, 4.96.

Dimethyl 2-(4-methylphenyl)cyclopropane-1,1-dicarboxylate. (4:1) 84% yield. IR (neat) 3021, 2957, 1745, 1443 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (s, 3H), 3.76 (s, 3H), 3.37 (s, 3H), 3.19 (dd, 1H, *J*=9.0, 7.5 Hz), 2.29 (s, 3H), 2.16 (dd, 1H, *J*=7.5, 5.0 Hz), 1.71 (dd, 1H, *J*=9.0, 5.0 Hz); ^{13}C NMR ($CDCl_3$) δ 170.1, 166.9, 136.8, 131.3, 128.7, 128.1, 52.6, 52.0, 37.0, 32.2, 20.9, 19.0. Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.98; H, 6.51.

Dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate. (3:1) 69% Yield. IR (neat) 3009, 2962, 2839, 1731, 1620, 1514, 1444, 1344, 1289, 1252, 1141, 1039, 850 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, 2H, *J*=8.4 Hz), 6.77 (d, 2H, *J*=8.4 Hz), 3.75 (s, 3H), 3.74 (s, 3H), 3.35 (s, 3H), 3.15 (dd, 1H, *J*=9.2, 8.6 Hz), 2.12 (dd, 1H, *J*=8.6, 5.1 Hz), 1.69 (dd, *J*=9.2, 5.1 Hz); ^{13}C NMR ($CDCl_3$) δ 170.3, 167.1, 158.9, 129.6, 126.4, 113.5, 55.1, 52.7, 52.2, 37.0, 32.1, 19.2. Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10. Found: C, 63.72; H, 6.14.

Methyl 2β-butyl-1β-phenylcyclopropane-1α-carboxylate. (99:1) 82% yield. IR (neat) 2955, 2867, 1719 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.25 (m, 5H), 3.60 (s, 3H), 1.83–1.78 (m, 1H), 1.69 (dd, 1H, *J*=8.5, 3.7 Hz), 1.38–1.34 (m, 3H), 1.27–1.20 (m, 2H), 1.08 (dd, 1H, *J*=6.1, 3.7 Hz), 0.80 (t, 3H, *J*=7.3 Hz), 0.53–0.45 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 175.2, 136.4, 131.4, 127.9, 127.0, 52.0, 33.4, 31.2, 29.8, 28.5, 22.2, 21.5, 13.8. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.61; H, 8.74.

Methyl 2β-butoxy-1β-phenylcyclopropane-1α-carboxylate. (1:99–2.5:97.5) 84% yield. IR (neat) 2955, 2867, 1719 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (m, 5H), 3.93 (dd, 1H, *J*=6.9, 4.5 Hz), 3.63 (s, 3H), 3.60 (q, 2H, *J*=6.0 Hz), 1.79 (dd, 1H, *J*=7.2, 5.7 Hz), 1.61 (dd, 1H, *J*=10.5, 4.8 Hz), 1.87–1.80 (m, 2H), 1.10 (sextet, 2H, *J*=6.7 Hz), 0.76 (t, 3H, *J*=7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 173.4, 134.1, 131.3, 127.6, 126.7, 70.5, 64.7, 51.9, 34.8, 31.1, 20.6, 18.6, 13.4. Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.55; H, 8.07.

Methyl 2β-(4-trifluoromethylphenyl)-1β-phenylcyclopropane-1α-carboxylate. (9:1) 60% yield. IR (neat) 3025, 2951, 2850, 2253, 1923, 1721, 1620, 1438 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, 2H, *J*=8.1 Hz), 7.20–7.10 (m, 3H), 7.10–6.80 (m, 2H), 6.84 (d, 2H, *J*=8.1 Hz), 3.66 (s, 3H), 3.15 (dd, 1H, *J*=9.0, 6.8 Hz), 2.18 (dd, 1H, *J*=9.0, 5.1 Hz), 1.89 (dd, 1H, *J*=6.8, 5.1 Hz); ^{13}C NMR ($CDCl_3$) δ 173.8, 140.8 (q, *J*=1.4 Hz), 134.0, 131.7, 131.7, 128.3 (q, *J*=32.4 Hz), 128.1, 127.3, 124.5 (q, *J*=4.1 Hz), 124.1 (q, *J*=270.1 Hz), 52.7, 37.9, 32.4, 20.8. Anal. Calcd for $C_{18}H_{15}F_3O_2$: C, 67.50; H, 4.72. Found: C, 67.23; H, 4.80.

Methyl 2β-(4-chlorophenyl)-1β-phenylcyclopropane-1α-carboxylate. (5:95) 95% yield. Mp 68–70°C; IR (neat) 3031, 2954, 1713, 1336 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16–6.99 (m, 7H), 6.73 (m, 2H), 3.65 (s, 3H), 3.11 (dd, 1H, *J*=9.4. 7.3 Hz), 2.15 (dd, 1H, *J*=9.4, 4.9 Hz), 1.82 (dd, 1H, *J*=7.3, 4.9 Hz); ^{13}C NMR ($CDCl_3$) δ 174.1, 134.9, 134.2, 131.9, 131.7, 129.1, 127.7, 127.7, 127.1, 52.5,

37.3, 32.2, 20.5. Anal. Calcd for $C_{17}H_{15}ClO_2$: C, 71.21; H, 5.27. Found: C, 71.25; H, 5.26.

Methyl 1β,2β-diphenylcyclopropane-1α-carboxylate. (5:95) 95% yield. Mp 68–70°C; IR (neat) 3031, 2954, 1713, 1336 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.16–6.99 (m, 10H), 6.73 (m, 2H), 3.65 (s, 3H), 3.11 (dd, 1H, J=9.4, 7.3 Hz), 2.15 (dd, 1H, J=9.4, 4.9 Hz), 1.87 (dd, 1H, J=7.3, 4.9 Hz); ^{13}C NMR ($CDCl_3$) δ 174.3, 136.3, 134.7, 131.9, 128.0, 127.7 (2C), 127.0, 126.3, 52.6, 37.4, 33.1, 20.5. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.71; H, 6.52.

Methyl 2β-(4-methylphenyl)-1β-phenylcyclopropane-1α-carboxylate. (9:1) 60% yield. IR (neat) 3036, 2951, 1721, 1257 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.11 (m, 3H), 7.02 (dd, 2H, J=6.8, 3.6 Hz), 6.84 (d, 2H, J=8.0 Hz), 6.63 (d, 2H, J=8.0 Hz), 3.62 (s, 3H), 3.06 (dd, 1H, J=9.6, 6.8 Hz), 2.18 (s, 3H), 2.11 (dd, 1H, J=9.6, 4.8 Hz), 1.82 (dd, 1H, J=6.8, 4.8 Hz); ^{13}C NMR ($CDCl_3$) δ 174.4, 135.7, 134.8, 133.2, 131.9, 128.4, 127.8, 127.6, 126.9, 52.5, 37.1, 32.9, 20.8, 20.5. Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.93; H, 6.87.

Methyl 2β-butoxy-1β-phenylcyclopropane-1α-carboxylate. (9:1) 84% yield. IR (neat) 2955, 2867, 1719 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.31 (m, 5H), 3.93 (dd, 1H, J=6.9, 4.5 Hz), 3.63 (s, 3H), 3.60 (q, 2H, J=6.0 Hz), 1.79 (dd, 1H, J=7.2, 5.7 Hz), 1.61 (dd, 1H, J=10.5, 4.8 Hz), 1.87–1.80 (m, 2H), 1.10 (sextet, 2H, J=6.7 Hz), 0.76 (t, 3H, J=7.2 Hz); ^{13}C NMR ($CDCl_3$) d 173.4, 134.1, 131.3, 127.6, 126.7, 70.5, 64.7, 51.9, 34.8, 31.1, 20.6, 18.6, 13.4. Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.55; H, 8.07.

Methyl 2β-(4-methoxyphenyl)-1β-phenylcyclopropane-1α-carboxylate. (9:1) 95% yield. Mp 68–70°C; IR (neat) 3031, 2954, 1713, 1336 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.26–6.96 (m, 9H), 3.68 (s, 3H), 3.62 (s, 3H), 3.03 (dd, 1H, J=10.7, 9.3 Hz), 2.10 (dd, 1H, J=9.3, 4.8 Hz), 1.79 (dd, 1H, J=10.7, 4.5 Hz); ^{13}C NMR ($CDCl_3$) δ 174.3, 158.0, 134.8, 131.9, 128.9, 128.2, 127.6, 126.9, 113.1, 54.9, 52.5, 36.9, 32.6, 20.4. Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.54; H, 6.49.

Methyl 2β-(4-trifluoromethylphenyl)-1β-(4-methoxyphenyl)cyclopropane-1α-carboxylate. (4:1) 41% yield. IR (neat) 3025, 2957, 2842, 1724, 1615, 1518 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, 2H, J=8.0 Hz), 6.92 (d, 2H, J=8.5 Hz), 6.85 (d, 2H, J=8.0 Hz), 6.68 (d, 2H, J=8.5 Hz), 3.72 (s, 3H), 3.66 (s, 3H), 3.10 (dd, 1H, J=9.0, 7.0 Hz), 2.17 (dd, 1H, J=9.0, 5.0 Hz), 1.84 (dd, 1H, J=7.0, 5.0 Hz); ^{13}C NMR ($CDCl_3$) δ 174.2, 158.6, 140.9 (q, J=1.4 Hz), 132.8, 128.3 (q, J=32.4 Hz), 128.2, 126.0, 124.5 (q, J=4.0 Hz), 124.1 (q, J=270.1 Hz), 113.3, 55.0, 52.7, 37.2, 32.5, 21.2. HRMS (EI) calcd for $C_{19}H_{17}F_3O_3$, 350.1100, found 350.1130.

Methyl 2β-(4-chlorophenyl)-1β-(4-methoxyphenyl)cyclopropane-1α-carboxylate. (4:1) 88% yield. IR (neat) 3014, 2957, 2842, 1718 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.03 (d, 2H, J=8.5 Hz), 6.92 (d, 2H, J=8.5 Hz), 6.68 (d, 4H, J=8.5 Hz), 3.72 (s, 3H), 3.65 (s, 3H), 3.03 (dd, 1H, J=9.0, 7.0 Hz), 2.12 (dd, 1H, J=9.0, 5.0 Hz), 1.76 (dd, 1H, J=7.0, 5.0 Hz); ^{13}C NMR ($CDCl_3$) d 174.3, 158.4, 135.1, 132.8, 131.9, 129.2, 127.8, 126.2, 113.2, 55.0, 52.6, 36.7, 32.4, 20.9. HRMS (EI) calcd for $C_{18}H_{17}ClO_3$, 316.0872, found 316.0866.

Methyl 2β-phenyl-1β-(4-methoxyphenyl)cyclopropane-1α-carboxylate. (4:1) 46% yield. IR (neat) 3041, 2999, 2956, 2839, 1721, 1518 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.80–7.20 (m, 3H), 6.92 (d, 2H, J=9.0 Hz), 6.79–6.74 (m, 2H), 6.65 (d, 2H, J=9.0 Hz), 3.69 (s, 3H), 3.64 (s, 3H), 3.07 (dd, 1H, J=9.0, 7.0 Hz), 2.11 (dd, 1H, J=9.0, 5.0 Hz), 1.81 (dd, 1H, J=7.0, 5.0 Hz); ^{13}C NMR ($CDCl_3$) δ 175.0, 158.8, 136.8, 133.3, 128.4, 128.1, 127.1, 126.6, 113.5, 55.4, 53.0, 37.0, 33.6, 21.2. Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.56; H, 6.41.

Methyl 2β-(4-methylphenyl)-1β-(4-methoxyphenyl)cyclopropane-1α-carboxylate. (4:1) 58% yield. IR (neat) 3020, 2957, 2836, 1730 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.93 (d, 2H, J=8.5 Hz), 6.87 (d, 2H, J=8.0 Hz), 6.66 (dd, 4H, J=8.5, 8.0 Hz), 3.71 (s, 3H), 3.64 (s, 3H), 3.02 (dd, 1H, J=9.0, 7.0 Hz), 2.20 (s, 3H), 2.09 (dd, 1H, J=9.0, 5.0 Hz), 1.77 (dd, 1H, J=7.0, 5.0 Hz); ^{13}C NMR ($CDCl_3$) δ 174.6, 158.3, 135.7, 133.3, 132.8, 128.4, 127.9, 126.9, 113.1, 55.0, 52.5, 36.4, 33.0, 20.9, 20.8. HRMS (EI) calcd for $C_{19}H_{20}O_3$, 296.1418, found 296.1412.

Methyl 1β, 2β-(di-4-methoxyphenyl)cyclopropane-1α-carboxylate. (4:1) 60% yield. IR (neat) 3009, 2951, 2839, 1721, 1520, 1255 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.93 (d, 2H, J=9.0 Hz), 6.68 (d, 2H, J=9.0 Hz), 6.66 (d, 2H, J=9.0 Hz), 6.60 (d, 2H, J=9.0 Hz), 3.70 (s, 3H), 3.67 (s, 3H), 3.63 (s, 3H), 3.01 (dd, 1H, J=9.5, 7.5 Hz), 2.09 (dd, 1H, J=9.5, 4.5 Hz), 1.74 (dd, 1H, J=7.5, 4.5 Hz); ^{13}C NMR ($CDCl_3$) δ 174.6, 158.2, 157.9, 132.8, 128.9, 128.3, 126.8, 113.1, 113.0, 55.0, 54.9, 52.4, 36.2, 32.7, 20.7. HRMS (EI) calcd for $C_{19}H_{20}O_4$, 312.1389, found 312.1362.

General procedures for competition studies

An equimolar (5.0 equiv.: 5.0 equiv.) solution of styrene and alkene in solvent was stirred with Rh(II) catalyst (0.01 equiv.) at room temperature under an argon atmosphere. To this solution was added diazo (1 equiv., 0.09 M) in solvent over 5 min and the reaction mixture was then stirred for a further 3–4 h. The solvent was removed by reduced pressure. The ratio of the products was determined from ^1H NMR (500 MHz) of the crude reaction residue.

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