tectability limits. If it is assumed that 1% or less yield of glycol could be undetected at 0.04 M dioxetane concentration, then the *maximum* lifetime of the biradicals derived from trimethyl- and tetramethyl-1,2-dioxetane is calculated to be 7 ps from eq 2.

These results show that certain 1,4-dioxy biradicals may be discrete intermediates in the thermolysis of dioxetanes. However, even the more stable of these biradicals are very short lived. With increased methyl substitution, the trimethyl- and tetramethyl-1,4-dioxybutane biradicals cannot be trapped with 1,4-cyclohexadiene, and the lifetime is 7 ps or less. With an estimated vibrational lifetime of 0.1 ps for a 1,4-dioxybutane biradical, based on the C–C stretching frequency, the trimethyl- and tetramethyl-substituted biradicals may or may not be true intermediates. It is interesting to note that the 1,4-dioxybutane biradicals have much shorter lifetimes than the corresponding carbon-centered biradicals. For example, carbon-centered 1,4-diyls produced in photochemical reactions of ketones are estimated to have lifetimes in the microsecond to nanosecond region.[2]

Acknowledgment. We thank Dr. J. C. Scaiano and P. McGarry for determining the absolute rate and activation parameters for H-atom abstraction from 1,4-cyclohexadiene by *tert*-butoxy radical. This work was supported by National Science Foundation Grant CHE-8413738.

Articles

Samarium-Promoted Cyclopropanation of Allylic Alcohols

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The use of samarium/mercury amalgam in conjunction with diiodomethane or chloroiodomethane to generate samarium carbenoids for the efficient cyclopropanation of allylic alcohols is discussed. These hydroxyl-directed cyclopropanations occur under mild conditions and allow a wide range of substitution about both the olefin and the carbinol carbon in allylic alcohol substrates. High yields and high diastereoselectivities are observed for many substrates.

The cyclopropane structural unit is found in many naturally occurring substances and is often incorporated into other synthetically derived compounds of biological interest, including steroid analogues.[2] In addition, diastereoselectively generated cyclopropanes have proven to be useful synthons for further transformation to stereodefined cyclic and acyclic compounds.[3]

The most widely recognized methodology for the stereoselective generation of cyclopropanes is the Simmons–Smith reaction, which has a proven record of service.[4] While the Simmons–Smith cyclopropanation procedure is generally quite effective, it suffers from both harshness and inconvenience due to the inhomogeneity of the reaction mixture and low reactivity of zinc metal. For example, reaction times approaching 60 h in boiling ethyl ether are required in some cases.[4a] Variations of the zinc-promoted Simmons–Smith reaction have been introduced with some success. The Furukawa modification utilizing diethylzinc as a reductant has proven useful in many cases,[5] as has the protocol of Yamamoto, which employs triethylaluminum and diiodomethane.[6] The pyrophoric nature of diethylzinc and triethylaluminum utilized in these procedures renders them somewhat less attractive. Recently, dichlorocarbene reactions have been demonstrated to be highly diastereoselective.[7] However, this strategy and the Seyferth methodology[8] both suffer from the need for subsequent reduction of the halocyclopropanes produced in the reaction in cases where unfunctionalized cyclopropanes are desired. Thus, despite the many advantages of these existing methods, there still appears a need for methodology capable of producing variously substituted cyclopropanes in an even more highly selective fashion. Earlier we reported on the use of samarium amalgam/diiodomethane to cyclopropanate allylic alcohols in high yields, often with

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high diastereoselectivity.[9] After obtaining these encouraging preliminary results, we sought to further delineate the scope of this methodology.

We wished to examine several aspects of this reaction in order to determine the utility and limitations of the methodology. In particular, the effect of both the size and number of substituents about the olefin, substitution about the carbinol carbon, and the dihalomethane employed in the reaction were more thoroughly investigated. While determining the utility of this methodology, we also hoped to gain insight into the factors controlling stereochemistry in addition of the postulated samarium carbenoids to the substituted olefin. Herein we report the results of these studies, which serve to outline the scope of the samarium-promoted cyclopropanation methodology.

Results and Discussion

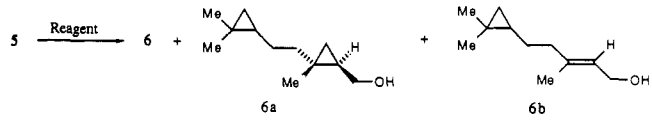
Our initial studies sought to exploit the samarium carbenoid implied as an intermediate in the generation of SmI_2 from samarium metal and diiodomethane[9,10] (eq 1).

$$Sm + CH_2I_2 \longrightarrow [\,ICH_2SmI\,] \longrightarrow SmI_2 + 0.5\ CH_2{=}CH_2 \qquad (1)$$

Due to the highly oxophilic nature of samarium, we postulated that the carbenoid might exhibit chemistry similar to that of zinc carbenoids; i.e., the production of hydroxyl-directed cyclopropanated products by reaction with allylic alcohols. While this was found to be the case, we were disturbed by the fact that small amounts of the allylic alcohol starting material often remained, even though 4-fold excesses of samarium and diiodomethane were utilized. In this study, we specifically probed the use of a carbenoid species generated from samarium and chloroiodomethane. We postulated that the decreased nucleofugacity of chloride ion relative to iodide ion would lead to a more stable carbenoid intermediate. This, in turn, should enhance yields of cyclopropane, since there is an inherent competition between cyclopropanation and α-elimination to ethylene in this process.

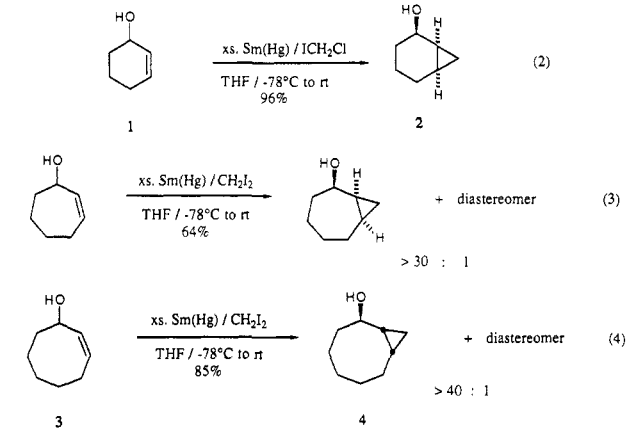
For cyclopropanations performed by using our methodology, typical reaction conditions involve addition of a solution of mercuric chloride in THF to a slurry of flame-dried samarium in THF, followed by addition of the allylic alcohol. After the reaction mixture is cooled to −78 °C, the dihalomethane is added dropwise. Regardless of the dihalomethane employed, the characteristic blue color of SmI_2 is observed as the temperature of the reaction mixture reaches −60 °C, and this color persists until quenching. The mercuric chloride appears to be helpful in initiating reactions at this low temperature. After approximately 2 h of stirring (once the reaction has warmed to room temperature), the reaction is quenched with saturated potassium carbonate. Standard extractive workup yields very clean crude material, which can be isolated by simple Kugelrohr distillation or, if necessary, flash chromatography to afford the pure cyclopropyl carbinol. The convenience and mildness of these conditions certainly surpass those of any of the methods mentioned above. In addition, exposure of the substrate to the SmI_2 reagent for extended periods of time appears to have no detrimental effect on either the isolated yield or diastereoselectivity of the product. This is not always the case with the Simmons–Smith reagent. Examples have been reported in which the yields of bicyclic alcohols produced from cyclopropanation of cyclic allylic alcohols by the Simmons–Smith procedure have decreased after increasing the time of exposure to the zinc reagent.[4e]

Scheme I



Reagent	% Yield 6	6a	6b
Et_2Zn / CH_2I_2	74	3	2
i-Bu_3Al / CH_2I_2	1	4	76
Sm(Hg) / ICH_2Cl	98	0	0

Stoichiometry studies established that 4 equiv of Sm/CH_2X_2 were required for complete consumption of the starting material. Utilizing this protocol, we investigated the cyclopropanation of several standard substrates. Probing the reactivity of these substrates allowed useful comparison of our method with others currently used and provided insight into the influence of the hydroxyl group in directing the incoming carbenoid. Equations 2–6 serve to outline the results of these cyclopropanations, which indicate that only the hydroxyl-directed products are observed in all cases. No traces of *trans*-bicyclo[4.1.0]heptan-2-ol were observed in the product mixture from cyclopropanation of 2-cyclohexen-1-ol (eq 2). This is also the case when the Simmons–Smith reagent is employed.[4e,4f] It is notable that in the case of 2-cyclohepten-1-ol, the samarium-based cyclopropanation provides much higher diastereoselectivity (eq 3) than that under the traditional Simmons–Smith conditions, where a 9:1 mixture of diastereomers results.[4e] Cyclopropanation of 2-cycloocten-1-ol with Sm(Hg)/CH_2I_2 shows comparable diastereoselectivity and the same sense of relative asymmetric induction as that achieved with Zn/CH_2I_2 (eq 4).[4e]



Methylenation of geraniol and nerol demonstrated that complete stereospecificity is achieved in the samarium-promoted cyclopropanation reactions (eq 5 and 6). Products formed from subjection of geraniol and nerol to

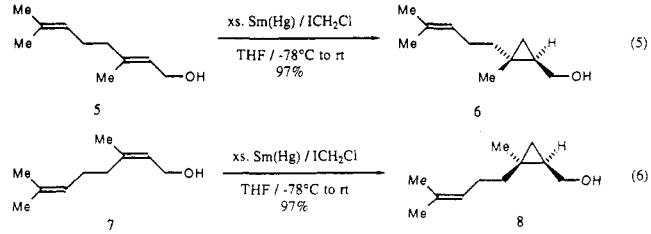


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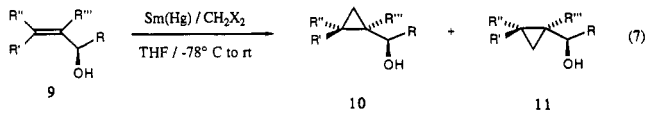
Table I. Cyclopropanation of Disubstituted (*E*)-Allylic Alcohols under Simmons-Smith Conditions

substrate	R	R′	R″	R‴	10:11
9a	Me	H	Me	H	57:43
9b	Me	H	Et	H	64:36
9c	Me	H	*t*-Bu	H	67:33

the $Sm(Hg)/ClCH_2I$ reaction conditions show no evidence of isomerization about the olefin undergoing cyclopropanation. Likewise, no products resulting from cyclopropanation at the C(6)–C(7) double bond of geraniol or nerol were observed. In fact, the samarium carbenoids appear to react exclusively with allylic alcohol substrates. Isolated olefins, homoallylic alcohols, and other functionalized olefinic substrates are inert to our standard reaction conditions.[9] This is contrary to results obtained from two of the alternative methods previously mentioned. The Simmons–Smith reagent and its variants provide approximately 5% of byproducts resulting from cyclopropanation at the isolated olefin in geraniol, while the Yamamoto methodology provides methylene transfer nearly exclusively at the remote olefin (Scheme I).[6] These results clearly demonstrate the high chemoselectivity exhibited by the samarium cyclopropanation methodology, as well as its complementarity to existing methods.

We proceeded to extend our previous study, probing the effect of substituents on diastereoselectivity. In the case of secondary allylic alcohols, two diastereomeric cyclopropyl carbinols are possible (eq 7). Stereochemistry of



(7)

the diastereomeric cyclopropyl carbinols was assigned by correlation through known procedures. Swern oxidation of the cyclopropyl carbinols to the corresponding acylcyclopropanes,[11] followed by reduction with lithium aluminum hydride, yielded authentic mixtures of alcohols **10** and **11**. The properties of these mixtures were compared to literature values of the product ratios and relative order of elution of the diastereomeric cyclopropyl carbinols observed after oxidation and reduction of similar, if not identical, substrates.[4g,12] We determined the degree of diastereoselectivity by injecting crude reaction mixtures onto fused silica capillary GC columns and compared these to the GC traces of the authentic mixtures of the diastereomeric cyclopropyl carbinols in order to determine if any of the minor diastereomer was present in the crude reaction mixture. In one case, **9p**, we were unable to separate the diastereomers by GC or HPLC and were forced to estimate the diastereomeric ratio from the ^{13}C NMR spectrum of the crude reaction mixture.

Previous studies on the Simmons–Smith reaction have focused mainly on the effect of R″ on diastereoselectivity in cyclopropanation of acyclic (*E*)-allylic alcohols (Table I).[4g] Studies performed by Pereyre and co-workers demonstrated little change in the ratio of products **10**:**11** as R″ was varied from methyl to *tert*-butyl in disubstituted (*E*)-allylic alcohols.

Likewise, we observed little diastereoselectivity in substrates from this series in which both R and R″ were relatively small alkyl groups (Table II). When R = Me,

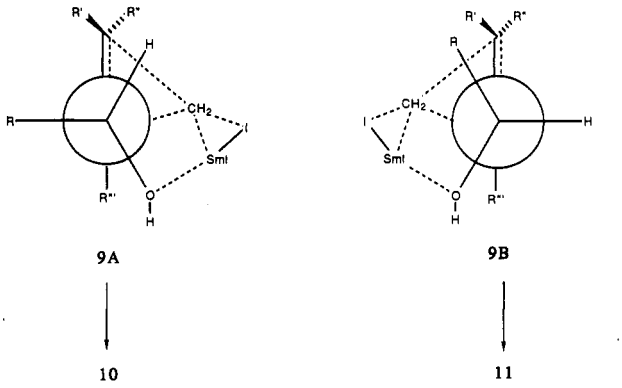


Figure 1. Possible transition structures for samarium-promoted cyclopropanation based on the Houk model.

essentially no stereoselectivity was observed, and the product ratio **10**:**11** remained close to unity. However, as R was increased in size from Me to *i*-Pr and *t*-Bu, product mixtures with quite high ratios of diastereomers (>200:1) of **10**:**11** were often isolated. These results appear to be quite consistent with the staggered (Houk) model[13] for the addition of carbenoids to olefins which was proposed in our preliminary study (Figure 1). For substrates in which R represents a small alkyl group in disubstituted (*E*)-allylic alcohols (R′ = H), there is apparently a small energy difference between the conformations represented as **9A** and **9B** in Figure 1. This leads to nearly random mixtures of the two diastereomeric cyclopropyl carbinols. However, as the steric bulk of R increases, the energy difference between conformations **9A** and **9B** increases accordingly. Diastereomer **10** becomes greatly favored because the large substituent R occupies the most favorable position antiperiplanar to the approaching carbenoid. It appears that the steric demands of R in this hydroxyl-complexed transition state dictate to a large extent the approach of the carbenoid moiety, and the nature of the carbenoid is purely secondary. In examples in which the reaction was carried out on disubstituted (*E*)-allylic alcohols with the $ClCH_2I/Sm(Hg)$ carbenoid in place of the carbenoid generated from $CH_2I_2/Sm(Hg)$, very little difference in yield or diastereoselectivity was observed (Table II).

While only a limited number of disubstituted (*Z*)-allylic alcohols were subjected to the reaction, all were cyclopropanated in good yield and with high diastereoselectivity (Table III). These results are quite consistent with those observed in the cyclopropanation of (*Z*)-allylic alcohols using Simmons–Smith methodology, in which diastereomeric ratios of **10**:**11** were reported to be >99:1.[4g] Again, these results support the predictions one can make by invoking the Houk model. Disubstituted (*Z*)-allylic alcohols can assume a transition-state conformation that minimizes interactions between R′ and R, while still allowing complexation between the hydroxyl group and the incoming carbenoid (Figure 1). These requirements would favor a transition state leading to carbinol **10**, in which R remains in a position antiperiplanar to the incoming carbenoid and steric interactions with R′ are minimized.

In order to define the degree to which the olefin could be substituted and still allow efficient cyclopropanation, we proceeded to subject several variously substituted allylic alcohols to the standard reaction conditions, and, where appropriate, determine the direction and extent of diast-

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Table II. Cyclopropanation of Disubstituted (*E*)-Allylic Alcohols with Sm(Hg)/CH_2X_2

substrate	R	R′	R″	R‴	CH_2I_2 ratio 10:11[a]	$ClCH_2I$ ratio 10:11[a]
9d	Me	H	Ph	H	1:6 (98)	1:1.3 (99)
9e	*n*-Bu	H	Ph	H	1:1.4 (99)[b]	–
9f	*i*-Pr	H	Ph	H	200:1 (88)	200:1 (82)
9g	*t*-Bu	H	Ph	H	200:1 (76)[b]	–
9h	Me	H	*t*-Bu	H	1:5.1 (98)[b]	–
9i	*i*-Pr	H	*t*-Bu	H	200:1 (46)[b]	–
9j	*i*-Pr	H	*n*-Bu	H	1.5:1 (74)	5:1 (93)

[a] Percent isolated yield in parentheses. [b] See ref 9.

Table III. Cyclopropanation of Disubstituted (*Z*)-Allylic Alcohols with Sm(Hg)/CH_2X_2

substrate	R	R′	R″	R‴	CH_2I_2 ratio 10:11[a]	$ClCH_2I$ ratio 10:11[a]
9k	Me	*n*-Bu	H	H	120:1 (36)	>45:1 (77)
9l	Me	*t*-Bu	H	H	200:1 (99)	>30:1 (80)
9m	Me	Ph	H	H	100:1 (62)	100:1 (67)

[a] Percent isolated yield in parentheses.

Table IV. Cyclopropanation of Variously Substituted Acyclic Allylic Alcohols with Sm(Hg)/CH_2X_2

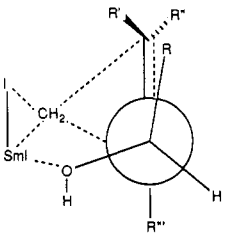
substrate	R	R′	R″	R‴	CH_2I_2 ratio 10:11[a]	$ClCH_2I$ ratio 10:11[a]
9n	Me	Me	$(CH_3)_2CCH(CH_2)_2$	H	50:1 (98)	200:1 (99)
9o	Me	$(CH_3)_2CCH(CH_2)_2$	Me	H	48:1 (31)	200:1 (98)
9p	Me	H	Et	Et	(59)	1:10 (67)
9q	Me	H	H	Ph	–	(21)

[a] Percent isolated yield in parentheses.

ereoselectivity in the cyclopropanation (Table IV).

As was observed for the disubstituted (*Z*)-allylic alcohols, high diastereoselectivity is achieved for both of the trisubstituted allylic alcohols bearing substituents (R′) cis to the carbinol (substrates **9n** and **9o**), with generally better yields observed when chloroiodomethane is employed in place of diiodomethane. There is some erosion in yields obtained for geminally disubstituted olefins. Steric crowding about the carbinol carbon is increased due to the presence of a substituent R‴, which appears to limit the efficiency of cyclopropanation (vide infra). In examples in which steric crowding is increased, chloroiodomethane is generally more effective than diiodomethane. This could be due to a longer lived chloroiodomethane carbenoid species, which would slow down decomposition of the carbenoid to ethylene. However, the greater steric demands of the approaching iodo-substituted carbenoid relative to the chloro-substituted carbenoid cannot be ruled out as a possible explanation for this phenomenon.

In the case of substrate **9p**, it appears that a slightly different transition state might be considered due to the presence of a substituent at R‴. In many respects, epoxidation reactions of allylic alcohols greatly resemble corresponding cyclopropanation reactions. In a study conducted by Chautemps and Pierre,[12c] the effects of substitution about an allylic alcohol on epoxidation were examined. A transition state was proposed for substrates with alkyl substituents at R‴ and small substituents at R. The transition state depicts R eclipsed with the olefin, and the hydroxyl and hydrogen groups gauche to R‴. A transition structure of this type applied to the current study would still allow complexation between the hydroxyl group and the samarium of the carbenoid, but would minimize any interactions between R and R‴ (Figure 2). Likewise, the transition state from the Houk model **9B** leading to diastereomer 11 (Figure 1) could also be invoked, since it also diminishes interactions between R and R‴. It is not clear to us at this time which of these transition states is operative, although both lead to a predominance of diastereomer 11.



9C

Figure 2. Possible transition structure for samarium-promoted cyclopropanation based on the Chautemps and Pierre model.

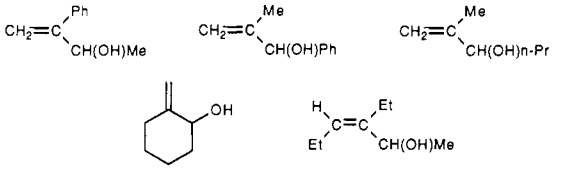


Figure 3. Allylic alcohols that provide poor yields of cyclopropanes under standard conditions.

In addition to the substrates mentioned above, several others were prepared and subjected to our general cyclopropanation reaction conditions. Figure 3 illustrates these substrates, for which isolated yields and diastereoselectivities were not determined because the reactions stopped far from completion under standard reaction conditions. In these cases, separation of products from starting material was not practical.

Due to the striking similarities between the results obtained employing Simmons–Smith methodology and samarium amalgam/dihalomethane methodology for other substrates, the failure of the Sm(Hg)/CH_2X_2 system to efficiently cyclopropanate 2-methylenecyclohexanol and related substrates was particularly surprising, since these are excellent substrates under Simmons–Smith conditions.[4f] These results, taken together with results from substrates **9p** and **9q** from Table IV, clearly indicate that geminal alkene substituents are detrimental to the cyclo-

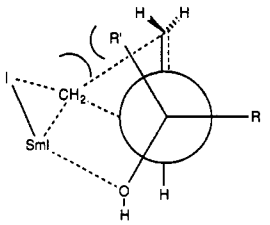
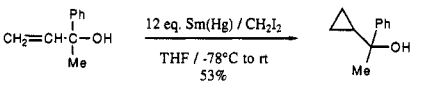


Figure 4. Steric interactions encountered in cyclopropanation of tertiary allylic alcohol substrates.

propanation. This appears to be a substitution pattern in which steric interactions between R and R′ or R‴ (Figures 1 and 2) provide sufficient steric crowding about the olefin to prohibit efficient cyclopropanation. These results support the steric interactions we have deemed relevant in the proposed transition states, and represent a case in which our results differ from those obtained under Simmons–Smith conditions.

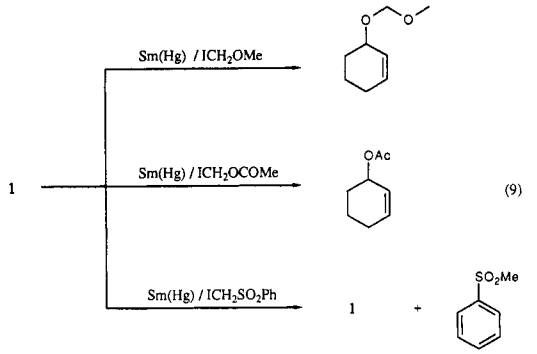
Another limitation of the samarium-promoted cyclopropanation methodology appears to be the extremely low yields obtained for tertiary alcohols, even those bearing no other substituents about the olefin. One such substrate (2-phenylbut-3-en-2-ol) was cyclopropanated, utilizing both chloroiodomethane and diiodomethane in only 14% and 9% yields, respectively, under the standard reaction conditions (4-fold excess of samarium metal and dihalomethane). However, treatment of 2-phenylbut-3-en-2-ol with 12 equiv of samarium and diiodomethane afforded the desired product in 53% yield (eq 8). According to our



(8)

proposed model, tertiary alcohols force the carbenoid to approach the olefin over an alkyl substituent of the fully substituted carbinol carbon (Figure 4). Decomposition of the carbenoid to ethylene might seriously compete with cyclopropanation of this highly hindered substrate. Thus, steric constraints of the transition state once again appear to inhibit efficient hydroxyl complexation and concomitant carbene addition. It is important to bear in mind that samarium-promoted cyclopropanation reactions *require* the presence of an allylic hydroxyl group, while the Simmons–Smith reaction is capable of cyclopropanating isolated double bonds. In addition, the zinc carbenoids are thermodynamically more stable than the samarium carbenoids. Taken together, it is clear that in more highly hindered allylic alcohol systems the traditional Simmons–Smith protocol offers some advantages.

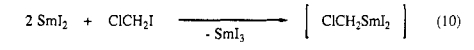
In attempts to devise alternative routes to the desired cyclopropanes, we examined use of appropriately functionalized monohalogenated compounds in conjunction with samarium. By incorporating a nonhalogen leaving group on the carbenoid precursor, we had hoped to modify the stability and reactivity of the carbenoid intermediate, as well as provide a handle for the introduction of chirality. Potential carbenoid precursors tested included iodomethyl acetate,[14] iodomethyl methyl ether,[15] and iodomethyl phenyl sulfone.[16] All of these reacted with Sm(Hg) as evidenced by the appearance of the characteristic color of Sm(II). However, products isolated by treatment of these potential carbenoid precursors with 2-cyclohexen-1-ol in the presence of Sm(Hg) were not the desired cyclopropyl carbinols, but rather derivatives of the alcohol in most cases (eq 9).



(9)

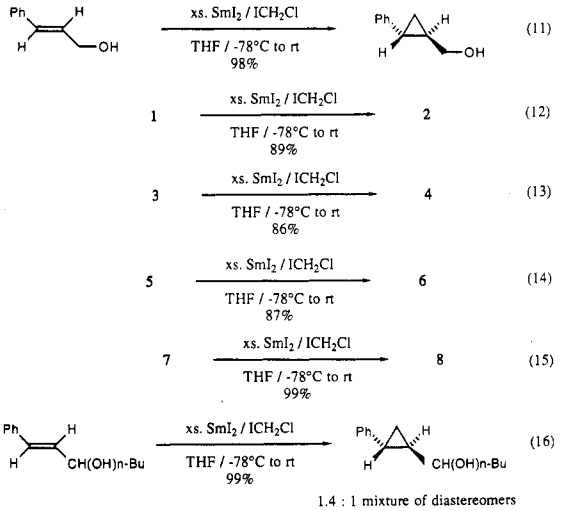
Attempts were also made to generate samarium-based halocarbenoids by reaction of samarium with several different multihalogenated methanes (e.g., CI_4, $CHBr_3$, and $BrCCl_3$) and to cyclopropanate olefins in a process analogous to the Seyferth methodology. Neither cyclohexene nor 2-cyclohexen-1-ol afforded the desired halocarbene addition products. The major products from attempts at cyclopropanation of 2-cyclohexen-1-ol with Sm(Hg)/$BrCCl_3$ included starting material, a 1:1 mixture of two unidentified products, and, in the case where 10 equiv of samarium and $BrCCl_3$ were employed, a small amount of *cis*-bicyclo[4.1.0]heptan-2-ol. This cyclopropane could have formed from initial cyclopropanation followed by reduction of the dihalocyclopropane by the samarium(II) species. The need for 4–5 equiv of samarium and the halocarbon creates a large excess of soluble SmX_2, a one-electron reductant capable of reducing organic halides to the corresponding hydrocarbons.[17]

We were intrigued by the possibility of generating "Sm(III) carbenoids" by reaction of SmI_2 with dihalomethanes, anticipating that these might possess desirable properties complementing the Sm(II) carbenoids (eq 10).



(10)

Imamoto and Takiyama had in fact generated Sm(III) carbenoids in their studies on cyclopropanation of enolates.[18] Somewhat to our surprise, the reactivity and selectivity of carbenoids generated from $SmI_2/ClCH_2I$ were virtually the same as that of Sm(Hg)/CH_2X_2 (eq 11–16).



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(18) Imamoto, T.; Takiyama, N. *Tetrahedron Lett.* **1987**, *28*, 1307.

While the question of whether the same species is involved in both cases is a matter of debate, from a practical point of view the protocol involving SmI_2 as a reductant (rather than samarium metal) is less desirable since more samarium and dihalomethane must be used to achieve complete conversion of allylic alcohol to product.

Finally, to the best of our knowledge no methodology exists which permits reliable Simmons–Smith type alkylidenation reactions with geminal dihalides other than 1,1-diiodomethane and 1,1-diiodoethane. We had previously utilized 1,1-diiodoethane/samarium amalgam as an efficient reagent for ethylidenation of 2-cyclohexen-1-ol and had found that this protocol proceeds with better endo/exo diastereoselectivity than is observed with the Simmons–Smith cyclopropanation.[9] In an attempt to extend this to other alkylidenations, homologous geminal dihaloalkanes were employed with samarium as carbenoid intermediates. The geminal dihalides investigated include 1,1-diiodopropane and 2,2-diiodopropane.[19] The allylic alcohol substrates could be recovered intact from these reactions, even though it was clear that the dihalides had reacted with the samarium metal. Rearrangement of carbenoids from such geminal dihalides is apparently very facile, affording alkene and intramolecular cyclopropane products in lieu of cyclopropanated allylic alcohols.[20]

Conclusions

Samarium carbenoids have proven effective in the cyclopropanation of cyclic and acyclic allylic alcohols. The procedure involved is extremely mild and convenient, with reaction times in the range of 2–3 h. Both chloroiodomethane and diiodomethane have been employed successfully, with chloroiodomethane proving to be more effective as steric crowding about the allylic alcohol increases.

The diastereoselectivity exhibited is high for disubstituted (*E*)-allylic alcohols with large substituents (R) on the allylic alcohol, as well as for disubstituted (*Z*)-allylic alcohols with virtually any alkyl substituents at R and R′. Trisubstituted olefins can be cyclopropanated efficiently as well, with high diastereoselectivity observed when R′ represents a bulky substituent. Yields are quite high for all substrates with the exception of disubstituted (*E*)-allylic alcohols with two large substituents, and alcohols with a high degree of steric bulk about the carbinol carbon.

A staggered (Houk) transition structure has been proposed to explain the observed diastereoselectivity. The highly oxophilic nature of samarium strongly suggests complexation between the samarium of the carbenoid and the hydroxyl group. The other substituents then occupy positions that simultaneously accommodate this need for complexation and minimize steric interactions.

The convenience, mildness, high diastereoselectivity, and exclusive reactivity with allylic alcohols provided by this methodology place it near the forefront of currently available methods for the cyclopropanation of cyclic and acyclic allylic alcohols.

Experimental Section

IR spectra were recorded on a Mattson-Polaris FT-IR spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on either a Magnachem A-200 or a Gemini-300 NMR instrument, operating at 200 and 300 MHz, respectively. $CDCl_3$ was employed as the solvent for both ^1H and ^{13}C NMR analyses, with $CHCl_3$ as reference for ^1H NMR spectroscopy and $CDCl_3$ as internal standard for ^{13}C NMR spectroscopy. Capillary GC traces were obtained from Hewlett-Packard Model 5890A gas–liquid chromatographs containing either a 25 m × 320 μm 5% phenyl SE-54 fused silica or 10% fused silica Carbowax column, with a Hewlett-Packard Model 3390 digital integrator. Low-resolution and exact mass spectra were recorded on a VG7070 EQ-HF instrument with perfluorokerosene as internal standard. Standard flash chromatography procedures were followed.[21]

Reagents. Tetrahydrofuran was distilled immediately prior to use from benzophenone ketyl under argon. Samarium metal was purchased from Research Chemicals, Phoenix, AZ, and was weighed and stored under an inert atmosphere. Diiodomethane and chloroiodomethane were purchased from Fluka Chemicals and distilled prior to use. Standard benchtop techniques were employed for handling air-sensitive reagents,[22] and all reactions were carried out under an argon atmosphere.

Starting Materials. The *trans*-4-phenyl-1-alken-3-ols were prepared by addition of an appropriate Grignard or organolithium reagent to cinnamaldehyde. Other disubstituted (*E*)-allylic alcohols were prepared by treatment of an appropriate alkyne with butyllithium,[23] addition of an aldehyde or ketone, followed by reduction with lithium aluminum hydride.[24] The disubstituted (*Z*)-allylic alcohols were prepared by reduction of the appropriate alkynol in the presence of $Ni(OAc)_2/NaBH_4$[25] poisoned with ethylenediamine. Substrates **9n** and **9o** were prepared by Swern oxidation[11] of nerol and geraniol, followed by addition of methyllithium to the unsaturated aldehyde. 2-Methylenecyclohexanol was prepared from a known literature procedure.[26] Substrate **9p** was prepared via hydroalumination of 3-hexyne,[27] followed by trapping the organoaluminate with acetaldehyde. (*Z*)-3-Ethyl-3-hexen-2-ol was prepared via hydroboration of 3-hexyne with catecholborane, followed by treatment with bromine and sodium methoxide to yield (*Z*)-3-bromo-3-hexene.[28] This was treated with 2 equiv of *t*-BuLi and 1 equiv of acetaldehyde to afford the desired allylic alcohol stereospecifically.[29]

Cyclopropanation of Allylic Alcohols Using Samarium/Dihalomethanes. General Procedure. To a dry 25-mL round-bottom flask equipped with stirbar was added the samarium metal (2.1 mmol, 0.316 g). The flask was simultaneously flushed with argon and flamed dry. To the cooled flask was added 5 mL of THF, followed by a solution of mercuric chloride (0.2 mmol, 0.054 g) in 5 mL of THF. This was allowed to stir for 10 min followed by addition of the allylic alcohol (0.5 mmol). The flask was cooled to −78 °C, and the dihalomethane (2.0 mmol) was added dropwise. The mixture was allowed to warm to room temperature and stir for an additional 1–2 h. The reaction was followed by TLC and GC. The reaction was quenched with saturated K_2CO_3 and extracted with ethyl ether. The ether layer was washed with brine three times, dried over K_2CO_3, filtered, and concentrated in vacuo to yield the crude material. Flash chromatography or Kugelrohr distillation yielded the pure cyclopropyl carbinol.

Cyclopropanation of 2-Cyclohexen-1-ol (1). According to the general procedure, 1 (1 mmol) was cyclopropanated to provide ***cis*-bicyclo[4.1.0]heptan-2-ol (2)** in 96% yield (0.107 g, 0.955 mmol) as a clear, colorless oil, isolated by flash chromatography on silica gel eluting with 2:1 hexanes–EtOAc. The isolated product was 99% pure as indicated by GLC analysis: ^1H NMR ($CDCl_3$) δ 4.26–4.04 (m, 1 H), 1.87–1.74 (m, 1 H), 1.65–1.53 (m, 2 H), 1.40–0.84 (m, 6 H), 0.59–0.48 (m, 1 H), 0.30–0.22 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 67.26, 29.83, 22.86, 20.78, 17.69, 12.76, 7.28; IR (neat) 3400, 3050, 2950, 2850, 1050, 1000 cm^{-1}; exact mass calcd for $C_7H_{12}O$ 112.0888, found 112.0874.

Cyclopropanation of 2-Cyclohepten-1-ol. According to the general procedure above, 2-cyclohepten-1-ol (0.92 mmol) was

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cyclopropanated to provide ***cis*-bicyclo[5.1.0]octan-2-ol**[46] in 64% yield (0.074 g, 0.59 mmol), isolated by flash chromatography on silica gel eluting with 1:1 hexanes–EtOAc: ^{1}H NMR ($CDCl_3$) δ 4.1 (m, 1 H), 1.25 (m, 11 H), 0.5 (m, 1 H), 0.4 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 71.14, 35.53, 28.44, 26.70, 24.89, 22.61, 14.75, 2.91.

Cyclopropanation of 2-Cycloocten-1-ol. According to the general procedure above, 2-cycloocten-1-ol (1.06 mmol) was cyclopropanated to provide ***trans*-bicyclo[6.1.0]nonan-2-ol**[46,30] in 85% GC yield (0.90 mmol) by reference to decane as an internal standard.

Cyclopropanation of Geraniol (5). The general procedure was followed to yield 97% (0.082 g, 0.487 mmol) of ***trans*-1-(hydroxymethyl)-2-methyl-2-(4-methyl-3-pentenyl)cyclopropane (6)** as a clear colorless oil after Kugelrohr distillation (55–65 °C at 0.1 mmHg). The isolated product was 94% pure as indicated by GLC analysis: ^{1}H NMR ($CDCl_3$) δ 5.11–5.08 (m, 1 H), 3.73–3.64 (dd, J = 11.4, 6.5 Hz, 1 H), 3.51–3.41 (dd, J = 11.4, 8.5 Hz, 1 H), 2.06–0.85 (m, 6 H), 1.64 (s, 3 H), 1.58 (s, 3 H), 1.06 (s, 3 H), 0.51–0.44 (m, 1 H), 0.12–0.07 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 131.37, 124.68, 63.96, 41.12, 26.30, 25.74, 25.54, 19.97, 17.73, 17.68, 17.11; IR (neat) 3415, 2930, 1450, 1385, 1034 cm^{-1}.

Cyclopropanation of Nerol (7). Via the general procedure described above, 7 was cyclopropanated to yield ***cis*-1-(hydroxymethyl)-2-methyl-2-(4-methyl-3-pentenyl)cyclopropane (8)** in 97% yield (0.081 g, 0.481 mmol) as a clear, colorless oil after Kugelrohr distillation. The isolated product was 97% pure as indicated by GLC analysis: ^{1}H NMR ($CDCl_3$) δ 5.31–5.10 (m, 1 H), 3.61–3.54 (m, 2 H), 2.30–2.10 (m, 2 H), 1.65 (b s, 3 H), 1.58 (s, 3 H), 1.52–1.19 (m, 2 H), 1.03 (s, 3 H), 0.94–0.82 (m, 1 H), 0.48–0.45 (dd, J = 8.7, 4.6 Hz, 2 H), 0.20–0.10 (t, J = 5.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 131.50, 124.60, 63.49, 34.16, 27.32, 25.72 (2), 24.32, 20.19, 17.51(2); IR (neat) 3335, 3055, 2925, 1450, 1380, 1085, 1030, 735 cm^{-1}; exact mass calcd for $C_{11}H_{20}O$: 168.1514, found 168.1508.

Cyclopropanation of (*E*)-4-Phenylbut-3-en-2-ol (9d). The general procedure for cyclopropanation was followed to afford two ***trans*-1-(1-hydroxyethyl)-2-phenylcyclopropane** diastereomers in 99% yield (0.081 g, 0.499 mmol) as a clear, colorless oil after Kugelrohr distillation: bp 50–60 °C (0.1 mmHg). The isolated product was 98% pure as indicated by GLC analysis: ^{1}H NMR ($CDCl_3$) δ 7.32–7.07 (m, 5 H), 3.37–3.24 (m, 1 H), 1.88–1.71 (m, 2 H), 1.39–1.04 (m, 5 H), 0.95–0.81 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 142.70, 128.39, 125.90, 125.63, 71.85, 30.89, 22.46, 21.41, 13.40; IR ($CDCl_3$) 3700, 3510, 2920, 1250, 1100, 1050 cm^{-1}; exact mass calcd for $C_{11}H_{14}O$ 162.1059, found 162.1045.

Cyclopropanation of (*E*)-2-Methyl-5-phenylpent-4-en-3-ol (9f). According to the general procedure, **9f** (0.070g, 0.397 mmol) was cyclopropanated to afford ***trans*-1-(1-hydroxy-2-methylpropyl)-2-phenylcyclopropane (10f)** in 82% yield (0.057 g, 0.325 mmol) as a clear, colorless oil after flash chromatography on silica gel, eluting with 5:1 hexanes–EtOAc. The isolated product was 99% pure as indicated by GLC analysis: ^{1}H NMR ($CDCl_3$) δ 7.13–6.87 (m, 5 H), 2.79–2.72 (dd, 1 H, J = 7.9, 6.1 Hz), 1.77–1.65 (m, 2 H), 1.45 (b s, 1 H), 1.30–1.10 (m, 2 H), 0.94–0.79 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 142.54, 128.56 (2), 125.89 (2), 125.81, 80.89, 34.36, 27.50, 21.83, 18.48, 18.23, 12.73; IR (neat) 3375, 3055, 2955, 2860, 1605, 1495, 1360, 1025 cm^{-1}; exact mass calcd for $C_{13}H_{18}O$ 190.1358, found 190.1377.

Cyclopropanation of (*E*)-2-Methylnon-4-en-3-ol (9j). According to the general procedure, **9j** (0.092 g, 0.589 mmol) was cyclopropanated to afford a 93% yield (0.093 g, 0.546 mmol) of ***trans*-1-(1-hydroxy-2-methylpropyl)-2-butylcyclopropane** as a clear, colorless oil, isolated as a 5:1 mixture of diastereomers by flash chromatography on silica gel, eluting with 7:1 hexanes–EtOAc. The isolated product was 99% pure as indicated by GLC analysis: ^{1}H NMR ($CDCl_3$) δ 2.90–2.80 (m, 1 H), 1.57–1.03 (m, 11 H), 0.94–0.83 (m, 5 H), 0.66–0.19 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 76.20, 39.51, 33.43, 31.76, 25.88, 22.56, 18.97, 17.07, 14.23, 14.11, 9.89; IR (neat) 3360, 2960, 2930, 2870, 1410, 1050 cm^{-1}; exact mass calcd for $C_{11}H_{20}$ (M – H_2O) 152.1565, found 152.1575.

Cyclopropanation of (*Z*)-3-Octen-2-ol (9k). According to the general procedure, **9k** (0.040 g, 0.312 mmol) was cyclopropanated to yield 77% (0.034 g, 0.239 mmol) of ***cis*-1-(1-hydroxyethyl)-2-butylcyclopropane (10k)** as a clear, colorless oil after flash chromatography on silica gel, eluting with 7:1 hexanes–EtOAc. The isolated product was 97% pure as indicated by GLC analysis: ^{1}H NMR ($CDCl_3$) δ 3.38–3.31 (m, 1 H), 1.50–0.90 (m, 10 H), 0.87–0.66 (m, 6 H), 0.06–0.01 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 69.28, 32.36, 28.57, 24.44, 23.64, 22.56, 16.48, 14.09, 9.89; IR (neat) 2950, 2910, 2860, 1450, 1175, 1100, 1050 cm^{-1}; exact mass calcd for C_9H_{16} (M – H_2O) 124.1265, found 124.1252.

Cyclopropanation of (*Z*)-5,5-Dimethylhex-3-en-2-ol (9l). According to the general procedure, **9l** (0.050 g, 0.39 mmol) was cyclopropanated to afford **10l** in 79% yield (0.044 g, 0.309 mmol) as a clear, colorless oil after flash chromatography on silica gel eluting with 7:1 hexanes–EtOAc. The isolated product was 97% pure as indicated by GLC analysis: ^{1}H NMR ($CDCl_3$) δ 3.75–3.66 (m, 1 H), 1.55 (b s, 1 H), 1.33 (d, J = 5.9 Hz, 3 H), 0.92 (s, 9 H), 0.89–0.23 (m, 4 H); ^{13}C NMR ($CDCl_3$)[31] δ 67.90, 30.38, 29.76, 29.27, 27.27, 24.02, 5.49; IR (neat) 3380, 2965, 2945, 1425 cm^{-1}.

Cyclopropanation of (*Z*)-4-Phenylbut-3-en-2-ol (9m). According to the general procedure above, **9m** (0.059 g, 0.398 mmol) was cyclopropanated to yield 67% (0.043 g, 0.265 mmol) of ***cis*-1-(1-hydroxyethyl)-2-phenylcyclopropane (10m)** as a white crystalline solid (mp 46–48 °C) after flash chromatography on silica gel, eluting with 5:1 hexanes–EtOAc. The isolated product was 97% pure as indicated by GLC analysis: ^{1}H NMR ($CDCl_3$) δ 7.24–7.01 (m, 5 H), 2.96–2.82 (m, 1 H), 2.24–2.12 (m, 1 H), 1.44 (b s, 1 H), 1.01–0.98 (d, J = 5.8 Hz, 3 H), 1.23–0.90 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 138.01, 128.68, 128.05, 125.97, 68.65, 26.76, 22.51, 20.95, 7.64; IR (neat) 3300, 1370, 1330, 900 cm^{-1}; exact mass calcd for $C_{11}H_{14}O$ 162.1045, found 162.1051.

Cyclopropanation of (*E*)-4-Methyl-4-(4-methyl-3-pentenyl)but-3-en-2-ol (9n). According to the general procedure shown above, **9n** (0.057 g, 0.339 mmol) was cyclopropanated to yield 99% (0.061 g, 0.334 mmol) of ***trans*-1-(1-hydroxyethyl)-2-methyl-2-(4-methyl-3-pentenyl)cyclopropane (10n)** as a clear, colorless oil after flash chromatography on silica gel, eluting with 9:1 hexanes–EtOAc. The isolated product was 94% pure as indicated by GLC analysis, as an 88:6 mixture of **10n:10o**:[32] ^{1}H NMR ($CDCl_3$) δ 5.11–5.03 (m, 1 H), 3.37–3.30 (m, 1 H), 2.06–1.94 (m, 3 H), 1.65 (s, 3 H), 1.58 (s, 3 H), 1.50 (b s, 1 H), 1.43–1.21 (m, 2 H), 1.27–1.24 (d, J = 5.8 Hz, 3 H), 1.03 (s, 3 H), 0.70–0.59 (dd, J = 8.8, 4.1 Hz, 1 H), 0.23–0.18 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 131.34, 124.60, 69.89, 41.61, 32.33, 25.83, 25.44, 23.73, 20.31, 18.43, 17.70; IR (neat) 3370, 2960, 1450, 1360, 1100, 1035, 960, 900 cm^{-1}; exact mass calcd for $C_{12}H_{20}$ (M – H_2O) 164.1565, found 164.1580.

Cyclopropanation of (*Z*)-4-Methyl-4-(4-methyl-3-pentenyl)but-3-en-2-ol (9o). Via the general procedure described above ***cis*-1-(1-hydroxyethyl)-2-methyl-2-(4-methyl-3-pentenyl)cyclopropane (10o)** was isolated in 98% yield (0.090 g, 0.494 mmol) as a clear, colorless oil after flash chromatography on silica gel, eluting with 9:1 hexanes–EtOAc. The isolated product was 100% pure as indicated by GLC analysis as a 91:9 mixture of **10o:10n**:[32] ^{1}H NMR ($CDCl_3$) δ 5.13–5.05 (m, 1 H), 3.46–3.35 (m, 1 H), 2.16–1.98 (m, 2 H), 1.66 (s, 3 H), 1.59 (s, 3 H), 1.30–1.27 (d, J = 6.4 Hz, 3 H), 1.01 (s, 3 H), 1.49–1.03 (m, 3 H), 0.72–0.61 (m, 1 H), 0.52–0.43 (m, 1 H), 0.27–0.22 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 131.54, 124.69, 69.15, 34.36, 33.73, 25.48, 24.24, 23.67, 20.47, 17.47, 17.44, 17.34; exact mass calcd for $C_{12}H_{20}$ (M – H_2O) 164.1565, found 164.1558.

Cyclopropanation of (*E*)-3-Ethylhex-3-en-2-ol (9p). According to the general procedure, **9p** was cyclopropanated to afford ***trans*-1-ethyl-1-(1-hydroxyethyl)-2-ethylcyclopropane**, which was isolated as a mixture of diastereomers in 77% yield (0.055 g, 0.387 mmol) as a clear, colorless oil after flash chromatography on silica gel, eluting with 3:1 hexanes–EtOAc. This isolated product was 97% pure as indicated by GLC analysis: ^{1}H NMR ($CDCl_3$) δ 3.29–3.20 (q, J = 6.4 Hz, 1 H), 1.42–1.13 (m, 4 H),

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(32) This ratio reflects the diastereomeric mixture of the starting allylic alcohol. Isomerization about the C(2)–C(3) bond occurred during the purification of both geranial and neral. As a result, the allylic alcohols **9n** and **9o** derived from these aldehydes were contaminated with minor amounts of the undesired diastereomer. Despite this complication, it was still possible to make structural assignments of the cyclopropyl carbinols by the standard oxidation/reduction procedure outlined in the text.

1.09–1.05 (d, J = 6.4 Hz, 3 H), 1.03–0.89 (m, 7 H), 0.63–0.53 (m, 1 H), 0.46–0.40 (dd, J = 8.8, 4.7 Hz, 1 H), 0.16 to –0.21 (m, 1 H); IR ($CDCl_3$) 3610, 3500, 2980, 2960, 2860, 1450, 1440, 1365, 1100, 1050, 1035, 1020, 905 cm^{-1}; exact mass calcd for C_9H_{17} (M – OH) 125.1330, found 125.1331.

Cyclopropanation of 3-Phenylbut-3-en-2-ol (9q). According to the general procedure, **9q** (0.087 g, 0.587 mmol) was cyclopropanated to afford the desired product, **1-(1-hydroxyethyl)-1-phenylcyclopropane** (0.020 g, 0.123 mmol, 21% yield), as a clear, colorless oil after flash chromatography on activity III aluminum oxide, eluting with 7:1 hexanes–EtOAc. The isolated product was 97% pure as indicated by GLC analysis: ^1H NMR ($CDCl_3$) 7.36–7.15 (m, 5 H), 3.40–3.31 (m, 1 H), 1.31 (b s, 1 H), 1.11–1.08 (d, J = 6.4 Hz, 3 H), 0.96–0.92 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 142.28, 131.87, 128.65, 127.43, 74.38, 33.03, 21.82, 11.81, 10.71; IR (neat) 3400, 2980, 1490, 1440, 1130, 1075, 1025, 935 cm^{-1}; exact mass calcd for $C_{11}H_{14}O$ 162.1044, found 162.1050.

Cyclopropanation of 2-Phenylbut-3-en-2-ol. The general procedure for cyclopropanation was followed to yield 14% (0.012 g, 0.073 mmol) of **1-phenyl-1-(1-hydroxyethyl)cyclopropane**, isolated by flash chromatography on activity III aluminum oxide, eluting with 3:1 hexanes–EtOAc. When the substrate (0.052 g, 0.344 mmol) was treated with a larger excess of Sm (0.655 g, 4.35 mmol) and CH_2I_2 (0.732 g, 4.10 mmol), the product could be isolated in 53% yield (0.030 g, 0.182 mmol), with 96% purity as indicated by GLC analysis: ^1H NMR ($CDCl_3$) δ 7.44–7.09 (m, 5 H), 1.38 (s, 3 H), 1.58–1.15 (m, 2 H), 0.50–0.28 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 148.06, 127.56 (2), 126.22 (2), 124.68, 72.00, 29.09, 22.71, 1.64, 0.98; IR (neat) 3420, 3050, 3000, 2955, 1500, 1450, 1375, 1030, 900 cm^{-1}; exact mass calcd for $C_{10}H_{11}O$ (M – CH_3) 147.0809, found 147.0802.

Cyclopropanation of Allylic Alcohols Using Samarium Diiodide/Dihalomethanes. General Procedure. To a dry 25-mL round-bottom flask equipped with stirbar was added the samarium metal (2.4 mmol, 0.3657 g). The flask was simultaneously flushed with argon and flamed dry. To the cooled flask (0 °C) was added 6 mL of THF, followed by 0.63 g (2.4 mmol) of CH_2I_2. This was allowed to stir for 1 h, and the allylic alcohol (0.30 mmol) was then added. After stirring for 15 min at room temperature, the flask was cooled to –78 °C, and 0.213 g (1.21 mmol) of ICH_2Cl was added dropwise. The mixture was allowed to react at –78 °C for 1.5 h and then was warmed slowly to room temperature and allowed to stir for an additional hour. The reaction was quenched with saturated K_2CO_3 and extracted with ethyl ether. The ether layer was washed with brine three times, dried over K_2CO_3, filtered, and concentrated in vacuo to yield the crude material. Flash chromatography or Kugelrohr distillation yielded the pure cyclopropyl carbinol.

Cyclopropanation of Cinnamyl Alcohol. According to the general procedure above, cinnamyl alcohol was cyclopropanated to provide 0.0439 g (98%) of product, identical in every respect with that prepared previously.[9]

Cyclopropanation of 1. According to the general procedure above, **1** (0.0263 g, 0.268 mmol) was cyclopropanated to provide 0.0268 g (89%) of **2**, identical in every respect with that prepared above.

Cyclopropanation of 3. According to the general procedure above, **3** (0.0282 g, 0.2234 mmol) was cyclopropanated to provide 0.027 g (86%) of **4**, identical in every respect with that prepared above.

Cyclopropanation of 5. According to the general procedure above, **5** (0.0386 g, 0.2502 mmol) was cyclopropanated to provide 0.0366 g (87%) of **6**, identical in every respect with that prepared above.

Cyclopropanation of 7. According to the general procedure above, **7** (0.0421 g, 0.273 mmol) was cyclopropanated to provide 0.0454 g (99%) of **8**, identical in every respect with that prepared above.

Cyclopropanation of (*E*)-1-Phenyl-1-hepten-3-ol. According to the general procedure above, the substrate (0.0452 g, 0.2375 mmol) was cyclopropanated to provide 0.0483 g (99%) of product as a 1.4:1 mixture of diastereomers, identical in every respect with that prepared previously.[9]

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Supplementary Material Available: ^1H NMR and ^{13}C NMR spectra for the products isolated from the cyclopropanations of **1**, **5**, **7**, and **9d,f,j–q** and capillary GLC analysis traces indicating the purity of the isolated compounds (39 pages). Ordering information is given on any current masthead page.