Reduction of Vinyloxiranes with Samarium Diiodide. An Efficient Route to Functionalized Chiral, Nonracemic (*E*)-Allylic Alcohols[1]

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Functionalized vinyloxiranes have been found to undergo facile reductive epoxide ring opening with samarium diiodide (SmI_2) in THF in the presence of a proton source to provide (*E*)-allylic alcohols. Reactions are exceedingly rapid, taking place in most cases at −90 °C within minutes. Ketones, esters, nitriles, and other functional groups survive these mild reaction conditions intact. Exclusive kinetic protonation of intermediates is observed. Furthermore, reactions take place under essentially neutral conditions, leading to exclusive generation of a single regio- and stereoisomeric (*E*)-allylic alcohol in nearly all cases. Unsaturated epoxide substrates for the reaction are readily available in chiral, nonracemic form, allowing unique access to optically active organic intermediates with an array of chemodifferentiable functionality useful for further elaboration.

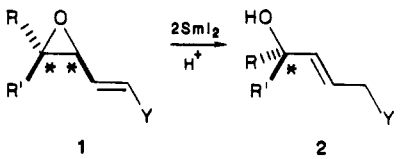
Development of synthetic methods which provide ready access to highly functionalized chiral, nonracemic substrates represents an important, continuing challenge for organic chemists. Perhaps the most significant contribution in this area during the past 10 years has been development of the Sharpless asymmetric epoxidation reaction.[2] This procedure provides straightforward access to a wide variety of optically active epoxy alcohols suitable for further transformation into useful organic products.[3]

We have previously reported on samarium diiodide (SmI_2) reduction of α,β-epoxy ketone substrates as a route to β-hydroxy ketones.[4] Utilizing the Sharpless asymmetric epoxidation technology[2] and complementary methodologies[5] to access requisite precursors, the SmI_2 reduction of α,β-epoxy ketones represents an efficient entry into chiral, nonracemic aldol products difficult to access by more conventional means. Samarium diiodide is an extraordinarily efficient, yet chemoselective reducing agent.[6] Recent studies have revealed that a variety of reductions[4,6,7] and coupling reactions[6,8] can be accomplished by SmI_2 in the presence of a wide range of functional groups. We sought to utilize the selective nature of SmI_2 to effect reduction of functionalized vinyloxirane derivatives, providing a unique route to potentially useful organic intermediates.

Three different reduction products of vinyloxiranes involving epoxide ring opening can be envisioned (Figure 1). Substitution of "hydride" at the epoxide terminus of the four-carbon unit followed by protonation (pathway a) provides an allylic alcohol, whereas S_N2 reactivity of "hydride" at the allylic site followed by protonation generates a homoallylic alcohol product (pathway b). Finally, S_N2' attack of "hydride" at the olefinic terminus (1,4-addition, pathway c) may lead to either (*E*)- or (*Z*)-allylic alcohols isomeric to those generated by pathway a.

All three reactivity patterns have been observed in simple substrates, although surprisingly few detailed studies have been conducted in attempts to bring about these useful reductions. Depending on substitution patterns of the substrate, $LiAlH_4$ has been observed to react at all three sites.[9] BH_3·THF and related reducing agents reduce unsaturated epoxides by pathway c to provide modest yields of (*Z*)-allylic alcohols,[10] and diisobutylaluminum hydride also reacts by this S_N2' fashion,[9c] although diastereoselectivity in this process is variable. Finally, $Ca/NH_3(l)$ and related dissolving metal reductions are reported to react with vinyloxiranes by an S_N2' process, providing (*E*)-allylic alcohol products (pathway c).[9c] In each of these methods studied to date, only alkyl or aryl substituents were present in the vinyloxirane substrates.

We believed that SmI_2 would be far more tolerant of sensitive functional groups (Y) incorporated into these



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substrates than hydride or dissolving metal reductions, and would therefore enjoy a broader scope of applicability in generation of substituted allylic alcohols. It was hoped that the SmI_2 methodology might provide advantages in terms of diastereoselectivity as well. Combined with the

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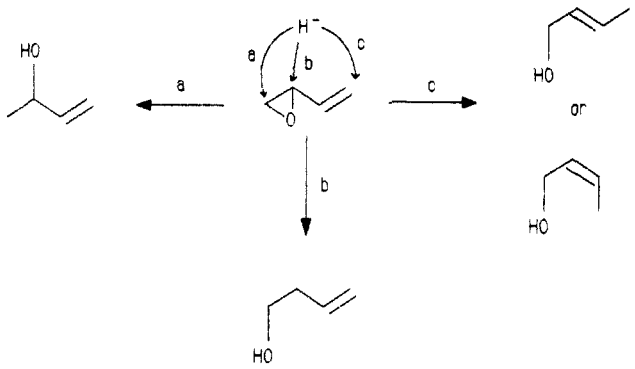


Figure 1.

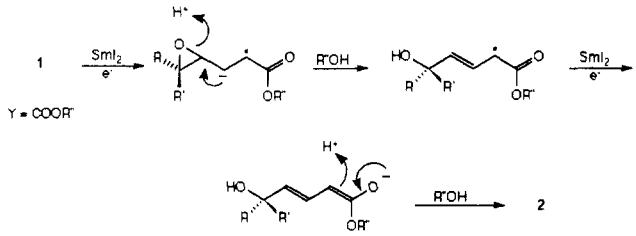
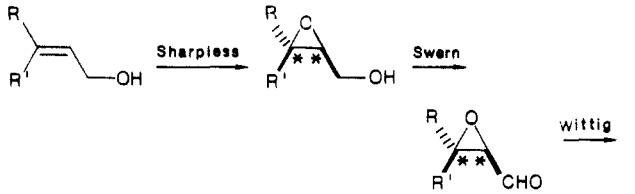


Figure 2.

Sharpless epoxidation reaction,[2] Swern oxidation,[11] and Wittig or Horner–Emmons chemistry,[12] such a reduction



would allow ready access to chiral, nonracemic organic intermediates with an array of chemodifferentiable functionality of great utility for further synthetic transformations.

Herein we describe our successful efforts to achieve this selective reduction with SmI_2.

Results and Discussion

At first glance, reduction of unsaturated epoxides to provide corresponding allylic alcohols with SmI_2 would appear to pose several significant problems. Although SmI_2 has been shown to react with isolated epoxides to generate olefins,[6a] reduction of vinyloxiranes to dienes was considered to be of minor concern. Our success in reducing α,β-epoxy ketones to β-hydroxy ketones without elimination to α,β-unsaturated ketones in the process[4] gave us confidence that this "deoxygenation" would not pose a significant problem in most cases.

Of greater concern was regio- and stereoselective generation of the olefin. Not only did the desired process require clean kinetic protonation of the intermediate (Figure 2), but neutral reaction conditions were required to prevent isomerization in those instances where conjugating groups (e.g. Y = –COR, –COOR, –CN, $-SO_2Ar$) were utilized in the starting materials. Furthermore, although mechanistic analogies to dissolving metal reductions of similar substrates could be made,[13] it was unclear what stereochemistry would be observed in the final products utilizing SmI_2 as the reductant.

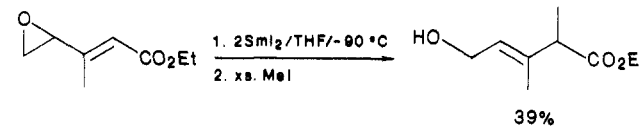
Finally, the scope of the reaction with respect to the types of groups Y that could be utilized in the reaction was of interest. While SmI_2 had previously been utilized to cleanly reduce unsaturated carboxylic acids and esters to saturated derivatives, nonselective reduction of α,β-unsaturated aldehydes and ketones resulted in mixtures of carbonyl and alcohol products.[6a] Furthermore, isolated double bonds remained unchanged in the presence of SmI_2, and so there was some question as to whether simple unsaturated epoxides (Y = H, alkyl) or those with electron-donating groups would be suitable substrates for reduction. Fortunately, nearly all of these concerns proved insignificant.

We initiated our studies utilizing unsaturated epoxy ester substrates. As mentioned above, unsaturated esters were known to be suitable substrates for SmI_2 reduction,[6a] and so effective reduction of the unsaturated epoxide by a mechanism similar to that depicted in Figure 2 was expected. Indeed, reactions in these cases were complete within seconds upon addition of substrates dissolved in THF/EtOH to SmI_2 in THF at –90 °C (Table I). Both the reaction and workup are operationally quite simple. Unsaturated epoxide substrates in THF/EtOH are added to a solution of SmI_2 in THF (samarium diiodide is generated in situ from samarium metal and 1,2-diiodoethane[14]). The reaction is quenched within 10 min at –90 °C by addition of a pH 8 buffer. Simple extraction and Kugelrohr distillation or flash chromatography provides pure allylic alcohols in excellent yields.

Elimination to dienes in this series poses little problem. In one instance (entry 6), minor amounts (<10%) of a less polar, more volatile product was detected that might be attributed to diene. This was easily removed from the desired alcohol by simple flash chromatography or Kugelrohr distillation. In all other examples crude reaction mixtures were void of these types of byproducts.

In nearly all cases, a single olefinic isomer was isolated from the reaction mixture (products in entries 8 and 10 are mixtures of geometric olefin isomers). In no case was more than 6% of α,β-unsaturated esters detected by capillary gas chromatography or 200-MHz ^1H NMR of crude reaction mixtures. Byproducts detected by capillary gas chromatography that might be attributable to any isomers were less than 3% in all but one case (entry 1). It is quite clear that *exclusive kinetic protonation of the intermediate ester dienolate* is realized[15] and that nearly neutral conditions are achieved in the reaction, inhibiting equilibration to more stable olefinic isomers.[16]

In one instance, we successfully trapped the dienolate intermediate with methyl iodide,[15] albeit in relatively low yields. Work continues in this area to improve yields in



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the alkylation, as well as to further expand the utility of this process by utilizing a number of different electrophilic quenching reagents.

Primary, secondary, and even sensitive tertiary allylic alcohol products could all be isolated cleanly and in high

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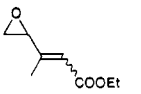
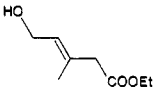
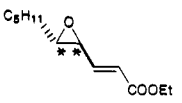
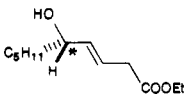
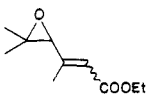
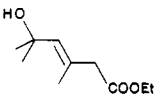
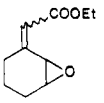
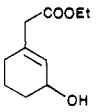
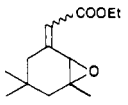
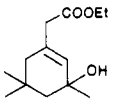
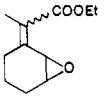
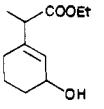
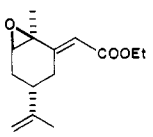
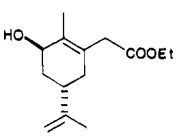
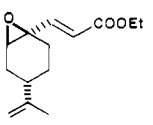
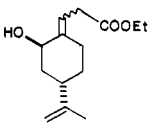
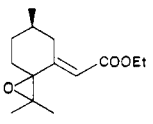
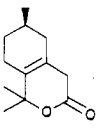
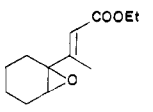
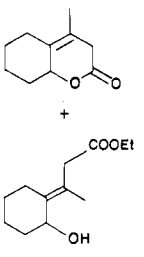
Table I. Reduction of Unsaturated Epoxyester Substrates with Samarium Diiodide[a]

entry	starting material	product	% isolated yield
1			77[b]
2			84
3			75
4			68
5			81
6			78[c]
7			81
8			79[d]
9			85
10			43 + 44

[a] All reactions were performed utilizing 2 equiv of SmI_2 in THF/EtOH at −98 °C. [b] α,β-unsaturated isomer was detected in 4% yield. [c] Diene was detected in 9% yield. [d] Inseparable mixture of *E* and *Z* olefinic isomers.

yield from reaction mixtures, further attesting to the mild reaction conditions. In those cases where formation of lactones is particularly favorable (entries 9 and 10), pure lactone or mixtures of lactone and hydroxy ester were isolated.

In one case (entry 2) we have established that chiral, nonracemic allylic alcohols can be readily accessed. Thus, Sharpless epoxidation[2,17] of (*E*)-2-octen-1-ol with Ti(OiPr)$_4$/*t*-BuOOH/L-(+)-diethyl tartrate led to a 78% isolated yield of (2*S*,3*S*)-2,3-epoxy-1-octanol (95% ee by capillary GLC analysis of the MTPA ester[18]). Swern oxidation[11] generated the desired aldehyde, which underwent smooth Horner–Emmons reaction[12] with triethyl phosphonoacetate/NaH in DME to provide the requisite unsaturated epoxy ester. Reduction with SmI_2 under standard conditions provided the desired allylic alcohol in 84% isolated yield. The product was determined to be 95% enantiomerically pure as measured by ^{1}H NMR in the presence of chiral shift reagent [Eu(hfc)$_3$],[19] indicating complete retention of absolute stereochemistry in the process within the limits of detection.

Table II. Reduction of Unsaturated Epoxide Substrates 3 with Samarium Diiodide[a]

starting material	Y	% isolated yield (4)
3a	-COOEt	68
3b	-CH=CHCOOEt	65[b]
3c	-CN	71
3d	-COMe	69

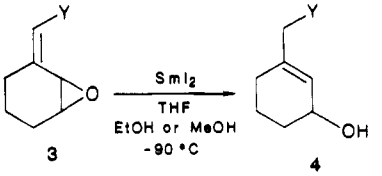
[a] All reactions were performed utilizing 2 equiv of SmI_2 in THF/ROH at −90 °C. [b] Product **4b** was exclusively the *E* olefinic isomer as determined by 200-MHz ^{1}H NMR.

Table III. Reaction of Unsaturated Epoxide Substrates 5 with Samarium Diiodide[a]

starting material	Y	% isolated yield (6)
5a	COSEt	80[b]
5b	SO_2Ph	82[c]
5c	$PO(OEt)_2$	84
5d	H	69[d]
5e	Me	42[e]
5f	SPh	54[f]

[a] All reactions were performed utilizing 2 equiv of SmI_2 in THF/ROH at −90 °C unless otherwise indicated. [b] Aldehyde detected in 4% yield. [c] δ-Hydroxy α,β-unsaturated sulfone detected in 5% yield. [d] Reaction performed at room temperature, with 9% triene generated. [e] Reaction performed at 0 °C, with triene generated in 32% yield. [f] Reaction performed at 0 °C.

Our attention next turned to determining the scope of the reaction with respect to substituents (Y) on the olefin. Several electron-withdrawing groups were found to serve admirably in the reaction with a standard substrate, including dienoate esters, nitriles, and ketones (Table II). In the case of the dienoate ester product (**4b**), only the (E) olefinic isomer (unconjugated with the ester functionality) was detected. We found no evidence for overreduction of the unsaturated ketone substrate (**3d**) under the conditions



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of the reaction. However, unsaturated epoxy aldehydes were not suitable substrates for the reaction, as complex mixtures of products resulted upon treatment with SmI_2.

The reaction proved to be much more general than we had at first anticipated. Not only were substrates with electron-withdrawing substituents on the olefin readily reduced, but the reaction was demonstrated to be applicable to a host of unsaturated epoxide substrates (Table III). Thus, phenylthio-substituted (**5f**), unsubstituted (**5d**), and alkyl-substituted (**5e**) vinyloxiranes are all ade-

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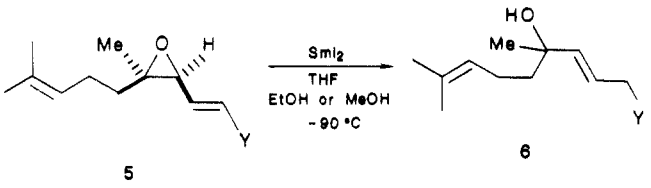

5 6

quate substrates for reduction, although in these cases reaction mixtures must be stirred at 0 °C or room temperature to effect complete reduction. Under these conditions, **5d** and **5e** provide significant amounts (9 and 32%, respectively) of triene products in addition to the desired allylic alcohol. (We have determined that these elimination products do not result from dehydration upon workup). Although the more polar alcohol products in these cases are readily separated from the epoxide deoxygenated products, for such unactivated vinyloxiranes the $Ca/NH_3(l)$ protocol[9c] would seem to be the preferred method for reduction.

The mechanism of reduction in instances where conjugating groups are present to facilitate electron transfer from SmI_2 to the vinyloxirane substrate may be quite different than those in which such groups are absent. Studies designed to elucidate the mechanism of these reactions and to determine, in particular, if "allylsamarium" species[20] might be implicated as intermediates in reactions lacking conjugating groups are currently underway.

Conclusion

We have demonstrated that reduction of a variety of functionalized vinyloxiranes with SmI_2 provides a highly efficient route to substituted allylic alcohols. The reaction is exceedingly rapid, taking place in most cases at −90 °C within minutes. Under these conditions, a wide range of functional groups can be tolerated, including ketones, esters, nitriles, sulfones, and phosphonates. Exclusive kinetic protonation (or alkylation) occurs, providing a single regio- and stereoisomeric product in nearly all cases. Reactions transpire under essentially neutral conditions, so that little or no equilibration to more stable olefinic isomers takes place. Finally, unsaturated epoxide substrates for the reaction are readily available in chiral, nonracemic form via a three-step procedure, providing easy access to optically active allylic alcohols that have great promise as synthons for further synthetic transformations.

Experimental Section

All boiling points and melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 727B spectrophotometer. ^1H NMR spectra were recorded at 200 MHz with $CDCl_3$ as solvent and $CHCl_3$ (δ 7.2) or Me_4Si (δ 0.00) as internal standard. ^{13}C NMR spectra were recorded at 50 MHz with $CDCl_3$ as both solvent and internal standard (δ 77.00). Capillary gas–liquid chromatographic analyses were performed with 25m SE-54 or OV-17 fused silica capillary columns. Flash chromatography was carried out under standard procedures.[21] Tetrahydrofuran (THF) was distilled from purple sodium benzophenone ketyl under argon immediately prior to use. Methanol was dried over 3-Å molecular sieves. All reactions were conducted under a positive pressure of argon, utilizing standard bench-top techniques for handling of air-sensitive materials.[22]

Reduction of Vinyloxiranes with SmI_2. General Procedure. To a slurry of Sm powder[23] (0.32 g, 2.1 mmol) in THF (2 mL) at room temperature under argon was added a solution of 1,2-diiodoethane[24] (0.56 g, 2.0 mmol) in THF (2 mL). The resultant olive-green slurry was stirred at ambient temperature for 1 h, after which time the resulting dark blue slurry of SmI_2 formed was cooled to −90 °C (liquid N_2, methanol) and treated with a solution of the vinyloxirane (1 mmol) in THF (2 mL) and MeOH (1 mL). The resultant brown reaction mixture was stirred for 5 min at −90 °C, quenched at this temperature by addition of pH 8 phosphate buffer, and then warmed to room temperature. The aqueous phase was extracted with Et_2O (5 × 3 mL), the combined extracts were dried ($MgSO_4/K_2CO_3$ or Na_2SO_4), and the volatiles were removed in vacuo.

Ethyl (*E*)-5-Hydroxy-3-methyl-3-pentenoate. With the general procedure above, ethyl 4,5-epoxy-3-methyl-2-pentenoate (0.156 g, 1.00 mmol) was reduced to provide 0.121 g (77%) of ethyl 5-hydroxy-3-methyl-3-pentenoate after flash chromatography (50% ethyl acetate in hexanes): IR (neat) 3400, 1720 cm^{-1}; ^1H NMR δ 5.54 (m, 1 H), 4.16 (m, 4 H), 3.03 (s, 2 H), 1.76 (s, 3 H), 1.26 (t, J = 7.2 Hz, 3 H); ^{13}C NMR δ 171.61, 131.92, 128.23, 60.64, 58.98, 44.78, 16.41, 14.11; exact mass calcd for $C_8H_{14}O_3$ 158.0943, found 158.0954.

Ethyl (5*S*)-(*E*)-5-Hydroxy-3-decenoate. With the general procedure above, ethyl (4*S*,5*S*)-(*E*)-4,5-epoxy-2-decenoate (0.218 g, 1.02 mmol) was reduced to provide 0.184 g (84%) of ethyl (5*S*)-(*E*)-5-hydroxy-3-decenoate after kugelrohr distillation: bp 90 °C (0.1 mmHg); IR (neat) 3400, 1730 cm^{-1}; ^1H NMR δ 5.73 (d of t, J = 15.5, 6.4 Hz, 1 H), 5.57 (dd, J = 15.5, 6.4 Hz, 1 H), 4.13 (m, 3 H), 3.03 (d, J = 6.4 Hz, 2 H), 1.8–0.8 (m, 15 H); ^{13}C NMR δ 187.0, 137.1, 123.1, 72.8, 61.0, 37.9, 37.5, 31.7, 25.0, 22.6, 14.4, 14.2; exact mass calcd for $C_{12}H_{22}O_3$ 214.1569, found 214.1582. ^1H NMR analysis ($CDCl_3$, 0.018 M, $CHOHCH_2$, Δδ 0.28) using Eu(hfc)$_3$, tris[3-((heptafluoropropyl)hydroxymethylene)-*d*-camphorato]europium(III), (1.5 equiv) as the chiral shift reagent[19] indicated a ≥95% enantiomeric excess.

Ethyl (*E*)-3,5-Dimethyl-5-hydroxy-3-hexenoate. With the general procedure above, ethyl (*E*)-3,5-dimethyl-4,5-epoxy-2-hexenoate (0.184 g, 1.00 mmol) was reduced to provide 0.140 g (75%) of ethyl (*E*)-3,5-dimethyl-5-hydroxy-3-hexenoate after flash chromatography (35% ethyl acetate in hexanes); IR (neat) 3450, 1720 cm^{-1}; ^1H NMR δ 5.44 (narrow m, 1 H), 4.13 (q, J = 7.2 Hz, 2 H), 2.93 (s, 2 H), 1.92 (d, J = 1.4 Hz, 3 H), 1.66 (br s, 1 H), 1.37 (s, 6 H), 1.25 (t, J = 7.2 Hz, 3 H); ^{13}C NMR δ 171.79, 136.42, 130.64, 70.80, 60.50, 46.14, 30.93, 17.26, 14.16; exact mass calcd for $C_{10}H_{18}O_3$ 186.1256, found 186.1247.

Ethyl (3-Hydroxy-1-cyclohexenyl)ethanoate. With the general procedure above, ethyl (7-oxabicyclo[4.1.0]hept-2-ylidene)ethanoate (0.179 g, 0.980 mmol) was reduced to provide 0.123 g (68%) of ethyl (3-hydroxy-1-cyclohexenyl)ethanoate after kugelrohr distillation: IR ($CDCl_3$) 3450, 1725 cm^{-1}; ^1H NMR δ 5.6 (m, 1 H), 4.1 (m, 3 H), 2.93 (narrow m, 2 H), 2.5–1.0 (m, 9 H); ^{13}C NMR δ 171.42, 134.67, 128.38, 65.43, 60.57, 42.97, 31.24, 28.37, 18.92, 14.05; exact mass calcd for $C_{10}H_{15}O_3$ (M^+ − 1) 183.1021, found 183.1031.

Ethyl (3-Hydroxy-3,5,5-trimethyl-1-cyclohexenyl)-ethanoate. With the general procedure above, ethyl (4,4,6-trimethyl-7-oxabicyclo[4.1.0]hept-2-ylidene)ethanoate (0.224 g, 1.00 mmol) was reduced to provide 0.183 g (81%) of ethyl (3-hydroxy-3,5,5-trimethyl-1-cyclohexenyl)ethanoate after kugelrohr distillation: IR (CCl_4) 3470, 1740 cm^{-1}; ^1H NMR δ 5.47 (narrow m, 1 H), 4.11 (q, J = 7.5 Hz, 2 H), 2.95 (s, 2 H), 1.80 (s, 2 H), 1.63 (d, J = 14.2 Hz, 1 H), 1.56 (s, 1 H), 1.49 (d, J = 14 Hz, 1 H), 1.24 (m, 6 H), 1.02 (s, 3 H), 0.94 (s, 3 H); ^{13}C NMR δ 171.25, 131.48, 130.88, 69.24, 60.53, 49.85, 43.18, 42.34, 30.93, 30.58, 30.31, 27.71, 14.14; exact mass calcd for $C_{13}H_{22}O_3$ 226.1568, found 226.1573.

Ethyl 2-(3-Hydroxy-1-cyclohexenyl)propanoate. With the general procedure above, ethyl 2-(7-oxabicyclo[4.1.0]hept-2-ylidene)propanoate (0.094 g, 0.48 mmol) was reduced to provide 0.074 g (78%) of ethyl 2-(3-hydroxy-1-cyclohexenyl)propanoate after flash chromatography (50% ethyl acetate in hexanes): IR 3460, 1740 cm^{-1}; ^1H NMR δ 5.63 (narrow m, 1 H), 4.20 (m, 1 H), 4.10 (q, J = 7.5 Hz, 2 H), 3.05 (m, 1 H), 2.2–1.0 (m, 13 H); ^{13}C

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NMR δ 174.31, 139.94, 126.42, 65.64, 60.43, 46.58, 31.58, 26.17, 19.22, 15.49, 14.06; exact mass calcd for $C_{11}H_{18}O_3$ 198.1256, found 198.1261.

Ethyl [(3*R*,5*S*)-(*E*)-3-Hydroxy-2-methyl-5-(2-propenyl)-1-cyclohexenyl]ethanoate. With the general procedure above, ethyl [(1*S*,4*S*,6*R*)-1-methyl-4-(2-propenyl)-7-oxabicyclo[4.1.0]hept-2-ylidene]ethanoate (0.235 g, 0.995 mmol) was reduced to provide 0.191 g (81%) of ethyl [(3*R*,5*S*)-(*E*)-3-hydroxy-2-methyl-5-(2-propenyl)-1-cyclohexenyl]ethanoate after flash chromatography (25% ethyl acetate in hexanes): IR (CCl_4) 3450, 1740 cm^{-1}; ^1H NMR δ 4.71 (narrow m, 2 H), 4.11 (q, J = 7.2 Hz, 2 H), 4.02 (m, 1 H), 3.03 (s, 2 H), 2.5–1.3 (m, 12 H), 1.23 (t, J = 7.2 Hz, 3 H); ^{13}C NMR δ 171.61, 148.76, 131.35, 127.16, 108.80, 69.27, 60.45, 38.74, 36.34, 35.80, 35.42, 20.68, 16.71, 13.98; exact mass calcd for $C_{14}H_{22}O_3$ 238.1569, found 238.1582.

Ethyl (*E*)- and (*Z*)-3-[(2*R*,4*S*)-2-Hydroxy-4-(2-propenyl)cyclohexylidene]propanoate. With the general procedure above, ethyl (*E*)-3-[(1*R*,4*S*,6*R*)-4-(2-propenyl)-7-oxabicyclo[4.1.0]hept-1-yl]propenoate (0.116 g, 0.490 mmol) was reduced to provide 0.093 g (79%) of ethyl 3-[(2*R*,4*S*)-2-hydroxy-4-(2-propenyl)cyclohexylidene]propanoate after flash chromatography (33% ethyl acetate in hexanes) as a mixture of (*E*)- and (*Z*)-isomers: IR (CCl_4) 3450, 1740 cm^{-1}. Ethyl (*E*)-3-[(2*R*,4*S*)-2-hydroxy-4-(2-propenyl)cyclohexylidene]propanoate: ^1H NMR δ 5.51 (dt, J = 7.0, 1.6 Hz, 1 H), 4.67 (narrow m, 2 H), 4.31 (m, 1 H), 4.12 (q, J = 7.0 Hz, 2 H), 3.05 (dd, J = 7.0, 1.1 Hz, 2 H), 2.7–1.1 (m, 14 H); ^{13}C NMR δ 171.92, 149.44, 143.47, 116.47, 108.82, 73.92, 60.69, 38.95, 38.47, 32.77, 31.84, 23.92, 20.93, 14.21. Ethyl (*Z*)-3-[(2*R*,4*S*)-2-hydroxy-4-(2-propenyl)cyclohexylidene]-propanoate: ^1H NMR δ 5.82 (dt, J = 7.5, 2.0 Hz, 1 H), 4.66 (m, 3 H), 4.11 (q, J = 7.2 Hz, 2 H), 3.17 (ddd, J = 16.3, 7.5, 1.6 Hz, 1 H), 2.99 (ddd, J = 16.3, 7.5, 1.0 Hz, 1 H), 2.52 (m, 2 H), 2.5–1.3 (m, 12 H); ^{13}C NMR δ 172.30, 149.63, 144.04, 115.64, 108.69, 64.97, 60.93, 38.41, 38.15, 32.42, 31.62, 20.90, 14.13. Exact mass calcd for $C_{14}H_{22}O_3$ 238.1569, found 238.1573.

(6*R*)-1,4,5,6,7,8-Hexahydro-1,1,6-trimethyl-3*H*-2-benzopyran-3-one. With the general procedure above, ethyl (6*R*)-(2,2,6-trimethyl-1-oxaspiro[2.5]oct-4-ylidene)ethanoate (0.231 g, 0.970 mmol) was reduced to provide 0.160 g (85%) of (6*R*)-1,4,5,6,7,8-hexahydro-1,1,6-trimethyl-3*H*-2-benzopyran-3-one after recrystallization from hexanes: mp 81–82 °C; IR 1720 cm^{-1}; ^1H NMR δ 2.83 (narrow m, 2 H), 2.3 (m, 16 H); ^{13}C NMR δ 170.2, 131.55, 122.71, 85.15, 37.31, 34.62, 30.93, 28.20, 27.25, 26.86, 24.62, 21.36; exact mass calcd for $C_{12}H_{18}O_2$ 194.1307, found 194.1338.

3,5,6,7,8,8a-Hexahydro-4-methyl-2*H*-1-benzopyran-2-one and Ethyl (*E*)-3-(2-Hydroxycyclohexylidene)butanoate. With the general procedure above, ethyl (*E*)-3-(7-oxabicyclo-[4.1.0]hept-1-yl)-2-butenoate (0.100 g, 0.476 mmol) was reduced to provide 0.034 g (43%) of 3,5,6,7,8,8a-hexahydro-4-methyl-2*H*-1-benzopyran-2-one and 0.045 g (44%) of ethyl (*E*)-3-(2-hydroxycyclohexylidene)butanoate after flash chromatography (50% ethyl acetate in hexanes). 3,5,6,7,8,8a-Hexahydro-4-methyl-2*H*-1-benzopyran-2-one: IR (CCl_4) 1745 cm^{-1}; ^1H NMR δ 4.69 (m, 1 H), 2.92 (m, 2 H), 2.73 (m, 1 H), 2.23 (m, 1 H), 2.0–1.0 (m, 9 H); ^{13}C NMR δ 168.72, 128.02, 117.78, 81.47, 35.50, 34.56, 27.37, 26.17, 24.38, 16.89; exact mass calcd for $C_{10}H_{14}O_2$ 166.0994; found 166.0996. Ethyl (*E*)-3-(2-Hydroxycyclohexylidene)butanoate: IR (CCl_4) 3450, 1740 cm^{-1}; ^1H NMR δ 4.78 (m, 1 H), 4.07 (q, J = 7.2 Hz, 2 H), 3.02 (s, 2 H), 2.5–1.1 (m, 15 H); ^{13}C NMR δ 171.85, 137.70, 121.44, 66.20, 60.47, 39.62, 33.65, 27.10, 25.45, 19.91, 18.49, 14.11; exact mass calcd for $C_{12}H_{20}O_3$ 212.1412, found 212.1425.

Ethyl (*E*)-4-(3-Hydroxy-1-cyclohexenyl)-3-butenoate. With the general procedure above, ethyl 4-(7-oxabicyclo[4.1.0]hept-2-ylidene)-2-butenoate (0.205 g, 0.984 mmol) was reduced to provide 0.135 g (65%) of ethyl (E)-4-(3-hydroxy-1-cyclohexenyl)-3-butenoate after flash chromatography (50% ethyl acetate in hexanes): IR (CCl_4) 3450, 1740 cm^{-1}; ^1H NMR δ 6.10 (d, J = 15.5 Hz, 1 H), 5.73 (dt, J = 15.5, 7.5 Hz, 1 H), 5.70 (m, 1 H), 4.26 (m, 1 H), 4.12 (q, J = 7.2 Hz, 2 H), 3.10 (d, J = 7.5 Hz, 2 H), 2.12 (m, 2 H), 1.82 m, 2 H), 1.54 (m, 3 H), 1.24 (t, J = 7.2 Hz, 3 H); ^{13}C NMR δ 171.65, 137.48, 135.91, 130.40, 120.47, 65.97, 60.56, 38.09, 31.82, 24.25, 18.84, 14.00; exact mass calcd for $C_{12}H_{18}O_3$ 210.1256, found 210.1273.

(3-Hydroxy-1-cyclohexenyl)ethanenitrile. With the general procedure above, (7-oxabicyclo[4.1.0]hept-2-ylidene)ethanenitrile (0.134 g, 0.988 mmol) was reduced to provide 0.097 g (71%) of (3-hydroxy-1-cyclohexenyl)ethanenitrile after flash chromatography (50% ethyl acetate in hexanes): IR (CCl_4) 3400, 2260, 2230 cm^{-1}; ^1H NMR δ 5.79 (m, 1 H), 4.18 (m, 1 H), 2.99 (s, 2 H), 2.40 (br s, 1 H), 2.0–1.5 (m, 6 H); ^{13}C NMR δ 130.61, 128.69, 116.99, 65.16, 30.98, 27.93, 25.22, 18.79; exact mass calcd for $C_8H_{11}NO$ 137.0841, found 137.0837.

3-(2-Oxopropyl)-2-cyclohexen-1-ol. With the general procedure above, 2-(2-oxopropylidene)-7-oxabicyclo[4.1.0]heptane (0.152 g, 1.0 mmol) was reduced to provide 0.124 g (69%) of 3-(2-oxopropyl)-2-cyclohexen-1-ol after flash chromatography (50% ethyl acetate in hexanes): IR (neat) 3380, 1700 cm^{-1}; ^1H NMR δ 5.6 (narrow m, 1 H), 4.2 (m, 1 H), 3.1 (s, 2 H) 2.1 (s, 3 H), 2.0–1.1 (m, 7 H); ^{13}C NMR δ 207.18, 134.22, 128.99, 65.29, 52.31, 31.16, 29.26, 28.50, 18.86; exact mass calcd for $C_9H_{14}O_2$ 154.0994, found 154.0968.

***S*-Ethyl (*E*)-5,9-Dimethyl-5-hydroxy-3,8-decadienethioate.** With the general procedure above, *S*-ethyl (4*R**,5*S**)-5,9-dimethyl-4,5-epoxy-2,8-decadienethioate (0.248 g, 0.984 mmol) was reduced to provide 0.201 g (80%) of *S*-ethyl (*E*)-5,9-dimethyl-5-hydroxy-3,8-decadienethioate after flash chromatography (50% ethyl acetate in hexanes); IR (neat) 3450, 1680 cm^{-1}; ^1H NMR δ 5.7 (m, 2 H), 5.1 (m, 1 H), 3.2 (m, 2 H) 2.85 (q, J = 7 Hz, 2 H), 2.3–1.0 (m, 16 H); ^{13}C NMR δ 197.78, 142.27, 131.65, 124.22, 119.09, 72.76, 46.98, 42.14, 27.74, 25.54, 23.20, 22.68, 17.55, 14.52; exact mass calcd for $C_{14}H_{24}O_2S$ 256.1497, found 256.1523.

(2*E*)-4,8-Dimethyl-4-hydroxy-1-(phenylsulfonyl)-2,7-nonadiene. With the general procedure above, (3*S**,4*R**)-(1*E*)-4,8-dimethyl-3,4-epoxy-1-(phenylsulfonyl)-1,7-nonadiene (0.306 g, 1.00 mmol) was reduced to provide 0.252 g (82%) of (2*E*)-4,8-dimethyl-4-hydroxy-1-(phenylsulfonyl)-2,7-nonadiene after flash chromatography (50% ethyl acetate in hexanes): IR (neat) 3500, 1315, 1155 cm^{-1}; ^1H NMR δ 7.9–7.5 (m, 5 H), 5.6 (m, 2 H), 5.05 (m, 1 H), 3.8 (d, J = 5 Hz, 2 H), 1.9 (m, 2 H), 1.7 (s, 3 H), 1.6 (s, 3 H), 1.5 (m, 2 H), 1.2 (s, 3 H); ^{13}C NMR δ 147.40, 137.96, 133.49, 131.55, 128.82, 128.23, 123.86, 113.57, 72.53, 59.38, 41.78, 27.45, 25.44, 22.35, 17.48; exact mass calcd for $C_{17}H_{23}O_3S$ 307.1368, found 307.1393.

Diethyl [(2*E*)-4,8-Dimethyl-4-hydroxy-2,7-nonadien-1-yl]phosphonate. With the general procedure above, diethyl [(3*R**,4*S**)-(1*E*)-4,8-dimethyl-3,4-epoxy-1,7-nonadien-1-yl]-phosphonate (0.233 g, 0.077 mmol) was reduced to provide 0.197 g (84%) of diethyl [(2*E*)-4,8-dimethyl-4-hydroxy-2,7-nonadien-1-yl]phosphonate after kugelrohr distillation: bp 100 °C (0.1 mmHg); IR (neat) 3400, 1250, 1040 cm^{-1}; ^1H NMR δ 5.7 (m, 2 H), 5.1 (m, 1 H), 4.1 (m, 4 H), 2.64 (d, J = 6 Hz, 1 H), 2.54 (d, J = 6 Hz, 1 H), 2.0 (m, 2 H), 1.8–1.2 (m, 19 H); ^{13}C NMR δ 142.33, 131.06, 124.19, 115.91, 72.17, 61.68, 42.08, 31.10, 28.30, 27.38, 25.31, 22.45, 17.29, 16.14; exact mass calcd for $C_{15}H_{30}O_4P$ 305.1882, found, 305.1904.

(2*E*)-4,8-Dimethyl-2,7-nonadien-4-ol. With the general procedure above, *cis*-2-methyl-2-(4-methyl-3-pentenyl)-3-ethenyl-1-oxacyclopropane (0.100 g, 0.60 mmol) was reduced at −78 °C for 30 min and then at 25 °C for 30 min to provide 0.070 g (69%) of (2*E*)-4,8-dimethyl-2,7-nonadien-4-ol after flash chromatography (20% ethyl acetate in hexanes): IR (neat) 3400 cm^{-1}; ^1H NMR δ 5.64 (dq, J = 16, 6 Hz, 1 H), 5.51 (d, J = 16 Hz, 1 H), 5.11 (m, 1 H), 2.00 (m, 2 H), 1.70 (d, J = 6 Hz, 3 H), 1.68 (s, 3 H), 1.59 (s, 3 H), 1.53 (m, 2 H), 1.25 (s, 3 H); ^{13}C NMR δ 137.96, 131.62, 124.45, 122.54, 72.86, 42.47, 27.94, 25.64, 22.88, 17.61; exact mass calcd for $C_{11}H_{20}O$ 168.1514, found 168.1511.

(3*E*)-5,9-Dimethyl-3,8-decadien-5-ol. With the general procedure above, *cis*-2-methyl-2-[4-methyl-3-pentenyl]-3-[1-propenyl]-1-oxacyclopropane (0.180 g, 1.00 mmol) was reduced at −90 °C for 30 min and then at 0 °C for 30 min to provide 0.077 g (44%) of (3*E*)-5,9-dimethyl-3,8-decadien-5-ol after flash chromatography (20% ethyl acetate in hexanes); IR (neat) 3400 cm^{-1}; ^1H NMR δ 5.65 (m, 1 H), 5.50 (d, J = 16 Hz, 1 H), 2.2–0.8 (m, 20 H); ^{13}C NMR δ 131.74, 125.69, 125.21, 122.16, 44.06, 39.94, 37.77, 32.10, 30.87, 29.06, 23.55, 22.72; exact mass calcd for $C_{12}H_{21}O$ (M^+ − 1) 181.1592, found 181.1582.

(2*E*)-4,8-Dimethyl-1-(phenylthio)-2,7-nonadien-4-ol. With the general procedure above, (3*R**,4*S**)-(1*E*)-4,8-dimethyl-3,4-epoxy-1-(phenylthio)-1,7-nonadiene (0.123 g, 0.448 mmol) was reduced at 0 °C for 30 min to provide 0.067 g (54%) of (2*E*)-4,8-dimethyl-1-(phenylthio)-2,7-nonadien-4-ol after flash chromatography (20% ethyl acetate in hexanes): IR (neat) 3430 cm^{-1};

^{1}H NMR δ 7.41 (m, 5 H), 5.81 (dt, J = 15.5, 6.4 Hz, 1 H), 5.65 (d, J = 15.5 Hz, 1 H), 5.15 (m, 1 H), 3.63 (d, J = 6.4 Hz, 2 H), 2.5-1.0 (m, 14 H); ^{13}C NMR δ 140.35, 135.69, 131.76, 130.27, 128.69, 126.25, 124.22, 122.81, 72.80, 42.16, 36.19, 27.99, 25.63, 22.66, 17.66; exact mass calcd for $C_{17}H_{24}OS$ 276.1547, found 276.1543.

Ethyl (*E*)-2,3-Dimethyl-5-hydroxy-3-pentenoate. To a slurry of Sm powder (0.160 g, 1.05 mmol) in THF (5 mL) at room temperature was added a solution of 1,2-diiodoethane (0.280 g, 1.00 mmol) in THF (5 mL). The resultant slurry was stirred at ambient temperature for 1 h, after which the slurry of SmI_2 formed was cooled to -90 °C and treated with a solution of ethyl (E)-4,5-epoxy-3-methyl-2-pentenoate, (0.075 g, 0.48 mmol), and iodomethane (0.5 mL) in THF (5 mL). The resultant mixture was stirred for 10 min at -90 °C, allowed to warm to room temperature, stirred for an additional 30 min at ambient temperature, and then quenched with pH 8 buffer. The aqueous phase was extracted with Et_2O, and the combined extracts were dried (Na_2SO_4) and then concentrated to provide 0.032 g (39%) of ethyl (*E*)-2,3-dimethyl-5-hydroxy-3-pentenoate after flash chromatography (50% ethyl acetate in hexanes): IR (neat) 3400, 1720 cm^{-1}; ^{1}H NMR δ 5.53 (m, 1 H), 4.10 (m, 4 H), 3.10 (q, J = 7.2 Hz, 1 H), 1.81 (br s, 1 H), 1.67 (narrow m, 3 H), 1.25 (m, 6 H); ^{13}C NMR δ 174.28, 137.35, 126.04, 60.56, 59.22, 48.15, 44.83, 15.66, 14.21 ppm; exact mass calcd for $C_9H_{16}O_3$ 172.1099, found 172.1091.

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Selective Reductions. 38. Reaction of Thexylchloroborane-Methyl Sulfide Complex in Methylene Chloride with Selected Organic Compounds Containing Representative Functional Groups. Comparison of the Reducing Characteristics of Thexylchloroborane, Thexylborane, and Diborane

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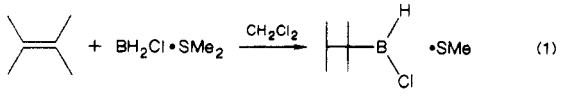
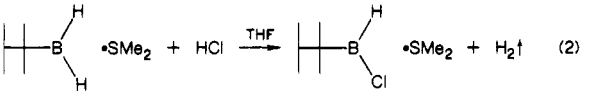
The approximate rate and stoichiometry of the reaction of excess thexylchloroborane-methyl sulfide complex, ThxBHCl·SMe_2, with 56 selected organic compounds containing representative functional groups under standard conditions (methylene chloride, 0 °C) were determined in order to define the characteristics of the reagent for selective reductions. The selectivity of the reagent was also compared to the selectivities of thexylborane and diborane. Alcohols and phenol react with the reagent at a fast rate to evolve an equivalent of hydrogen without any further reduction. Amines and aliphatic thiols do not form any hydrogen, while benzenethiol shows partial hydrogen formation. Aldehydes and ketones are reduced rapidly and quantitatively to give the corresponding alcohols. Unlike thexylborane and diborane, the reagent shows good stereoselectivity toward cyclic ketones. For example, 2-methylcyclohexanone is reduced to the less stable isomer, *cis*-2-methylcyclohexanol, in a high ratio (99.9% cis isomer at -78 °C). Cinnamaldehyde is reduced rapidly to cinnamyl alcohol, and any further reduction of the double bond is very slow under these conditions. *p*-Benzoquinone reacts only partially with the reagent while anthraquinone is totally unreactive. Carboxylic acids liberate 1 equiv of hydrogen rapidly and are further reduced to the corresponding aldehydes in good yields and purity. Acid chlorides react sluggishly with the reagent to use 2 equiv of hydride, while acetic anhydride utilizes 3 equiv of hydride to yield acetaldehyde and ethanol. On the other hand, cyclic anhydrides, such as succinic anhydride and phthalic anhydride, react very slowly with the reagent. Esters are almost inert toward thexylchloroborane. γ-Butyrolactone and phthalide are only partially reduced under the reaction conditions. Isopropenyl acetate utilizes 3 equiv of hydride to yield the corresponding acetaldehyde and presumably the hydroboration product of propylene. Only a partial reduction of epoxides can be observed. Primary amides like caproamide and benzamide evolve 1 equiv of hydrogen, but further reaction is very slow. Tertiary amides are almost inert under these conditions. Capronitrile reacts with the reagent to use 2 equiv of hydride in less than 24 h, while the reaction between benzonitrile and thexylchloroborane is sluggish. Nitrobenzene and 1-nitropropane do not react with the reagent, while azobenzene reacts only partially. Azoxybenzene consumes 2 equiv of hydride in 48 h. Only a sluggish reaction between thexylchloroborane and cyclohexanone oxime or phenyl isocyanate can be observed. Pyridine does not react, while pyridine *N*-oxide utilizes 3 equiv of hydride. Of the sulfur compounds tested, only dimethyl sulfoxide is reduced by the reagent to form the corresponding sulfide, while other sulfur compounds, such as disulfide, sulfide, and sulfone, are inert under these conditions. Although sulfonic acids evolve hydrogen, no further reduction is observed.

Thexylchloroborane can be prepared from the addition of 2,3-dimethyl-2-butene to monochloroborane-methyl sulfide in methylene chloride (eq 1). Preparation of



(1)

thexylchloroborane from thexylborane and hydrogen chloride has also been reported (eq 2).[2]



(2)

The reagent, ThxBHCl·SMe_2, in methylene chloride is very stable[3] and no disproportionation or loss of hydride is observed while the reagent is kept at 0 °C, at least for

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