Synthetically Useful β-Lithioalkoxides from Reductive Lithiation of Epoxides by Aromatic Radical Anions[1]

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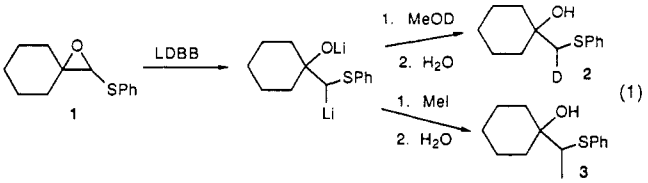
Epoxides are reductively cleaved by means of lithium 4,4′-di-*tert*-butylbiphenylide. Ethylene oxide itself cleaves to lithium 2-lithioethoxide (**15**) in less than 5 min at −95 °C. Epoxides possessing one unsubstituted carbon atom reduce in a matter of minutes at −78 °C. When both carbon atoms are monosubstituted, at least 1 h is required. Epoxides with one or with two geminal saturated substituents open mainly between the oxygen atom and the least substituted carbon atom. Ring opening in the other direction leads to an unstable β-lithioalkoxide which very rapidly forms an olefin. Acyclic 1,2-disubstituted epoxides yield only olefins. Cyclooctene oxide produces, after protonation, a 3:7 ratio of cyclooctanol and cyclooctene. Cyclohexene oxide gives a 3:1 ratio of cyclohexanol and cyclohexene. Vinyloxiranes, on the other hand, open at the most substituted C–O bond to produce an allylic anion associated with an alkoxide. The carbanionic centers of the resulting dianions add to the carbonyl groups of aldehydes and ketones; however, when a hydrogen atom is present on the carbon atom which is attached to both negatively charged atoms, some reduction of the carbonyl group competes with the nucleophilic addition. The allylic anions derived from vinyloxiranes, after treatment with titanium tetraisopropoxide or cerium(III) chloride, add to aldehydes mainly at the most or least substituted terminus, respectively. In the former case, the configuration of the resulting glycols is predominantly anti. A number of adducts of the dianions with conjugated unsaturated aldehydes and ketones can be converted to unsaturated cyclic 6-membered ring ethers in the presence of acid or methanesulfonyl chloride.

Introduction

Bartmann has reported that epoxides can be converted to β-metalloalkoxides via reductive metalation by metal naphthalenides and biphenylides.[2-4] During an attempt to produce α-lithioepoxides by reductive lithiation[5] of α-(phenylthio)epoxides using lithium 4,4′-di-*tert*-butylbiphenylide (LDBB),[6] we also discovered reductive cleavage of epoxides (eq 1).[7]

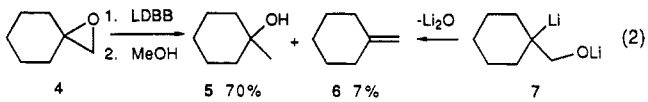


(1)

The present paper relates our attempts to clarify the nature and to delineate the scope and synthetic utility of this new type of reductive lithiation. Bartmann captured the dianions mainly by protonation and to a lesser extent by alkylation, sulfenylation, and carbonation.[2] We also protonated many of the dianions in order to gauge the rate and direction of the reductive cleavage and the stability of the dianions toward elimination. However, many of the dianions were treated with aldehydes and ketones, usually conjugated unsaturated ones in order to maximize the synthetic flexibility of the products.

Results and Discussion

1. General Characteristics and Mechanistic Aspects of Reductive Lithiation of Epoxides. In agreement with Bartmann's experience, we found that epoxides substituted with one alkyl group or with two alkyl groups attached to the same carbon atom open to produce the most substituted alkoxide (the least substituted carbanion, e.g. eq 2). This regiochemistry is also consistent with that found in Birch type reductions of epoxides.[3,8] However, in cases in which we sought it, we also found evidence for a minor degree of opening in the other sense. For example, reductive lithiation of **4** followed by a methanol quench produced not only alcohol **5** (70%) but about 7% of methylenecyclohexane (**6**), which very likely results from loss of Li_2O from the dianion **7** (eq 2). Barluenga has been



(2)

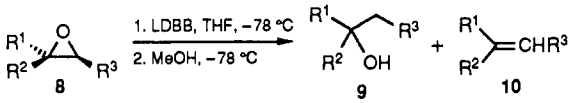
able to produce analogous dianions by reductive lithiation of β-chloroalkoxide ions and he has determined that only those in which the negative charge resides on a primary carbon atom are stable at −78 °C; the others split out lithium oxide very rapidly.[9] Not unexpectedly, 1-decene oxide (**8**; $R^1 = n\text{-}C_8H_{17}$, $R^2 = R^3 = H$) exhibited less regioselectivity than **4** upon reduction as indicated in Table I, which summarizes the results of the protonation experiments. In some of the experiments, a small portion of the putative dianion precursor of the olefin **10** ($R^1 = n\text{-}C_8H_{17}$, $R^2 = R^3 = H$) was inadvertently converted to 1-decanol when adequate precautions were not taken to rigorously dry the solvent (entry 6 is an example).

It is also evident from Table I that only an insignificant proportion of the olefin arises from loss of Li_2O from the dianion precursor of 2-decanol (**9**; $R^1 = n\text{-}C_8H_{17}$, $R^2 = R^3 = H$) since only a slightly greater ratio of olefin to 2-decanol is produced at the end of 60 min as compared to 2 min (entries 2–5). Since no 1-decanol is produced when

(1) Taken in part from the M.S. Thesis of Mohamed M. A. Awad, University of Pittsburgh, 1987.
(2) Bartmann, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 653.
(3) The only report, other than Bartmann's[2] of production of a detectable dianion from reductive metalation of an epoxide of an unfunctionalized olefin involves the reduction of styrene oxide with lithium in hexamethylphosphoric triamide; the product was quenched with D_2O. Kaiser, E. M.; Edmonds, C. G.; Grubb, S. D.; Smith, J. W.; Tramp, D. *J. Org. Chem.* **1971**, *36*, 330.
(4) Review of ether cleavages by alkali metals: Maercker, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 972.
(5) Cohen, T.; Bupathy, M. *Acc. Chem. Res.* **1989**, *22*, 152.
(6) Freeman, P.; Hutchinson, L. *J. Org. Chem.* **1980**, *45*, 1924.
(7) See footnote 6 of Bartmann's paper.[2]
(8) (a) Birch, A. J. *J. Proc. Roy. Soc. N. S. Wales* **1949**, *83*, 245. (b) Hallsworth, A. S.; Henbest, H. B. *J. Chem. Soc.* **1957**, 4604. Hallsworth, A. S.; Henbest, H. B. *J. Chem. Soc.* **1960**, 3571. (c) Brown, H. C.; Ikegami, S.; Kawakami, J. H. *J. Org. Chem.* **1970**, *35*, 3243. Benkeser, R. A.; Rappa, A.; Wolsieffer, L. A. *J. Org. Chem.* **1986**, *51*, 3391.
(9) (a) Barluenga, J.; Flórez, J.; Yus, M. *J. Chem. Soc., Perkin Trans. 1* **1983**, 3019. (b) Barluenga, J.; Fernández-Simón, J. L.; Concellón, J. M.; Yus, M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 3339. (c) Nájera, C.; Yus, M.; Seebach, D. *Helv. Chim. Acta* **1984**, *67*, 289.

0022-3263/90/1955-1528$02.50/0

Table I. Reductive Lithiation of Substituted Epoxides 8 with LDBB

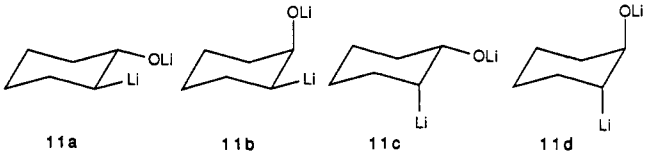


entry	R^1	R^2	R^3	t, min	relative GC yields,[a] % 8	9	10
1	n-C_8H_{17}	H	H	0.2	75	19	6
2				2	0	65	35
3				5	0	66	34
4				10	0	65	35
5				60	0	60	40
6				60	0	59	28[b]
7	c-C_6H_{11}	H	H	5	0	83	17
8	$-(CH_2)_5-$		H	5	0	90	10
9	n-C_4H_9	H	n-C_4H_9	5	94	0	6[c]
10				60	54	0	46[c]
11	H	n-C_4H_9	n-C_4H_9	60	34	0	66[d]
12	H	$-(CH_2)_4-$		30	26	56	18
13				60	0	75	25
14	H	$-(CH_2)_6-$		180	0	30	70[e]

[a] Absolute yields were typically 90%. [b] Slightly moist THF was used. 1-Decanol (3%) was also detected. [c] All trans. [d] 18% cis, 82% trans. [e] Configuration of alkene not determined.

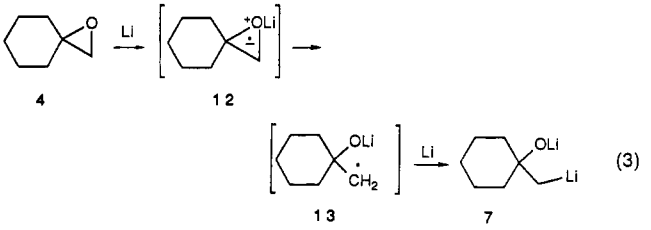
the reaction is quenched after only 0.2 min as long as dry THF is used as solvent (entry 1), it appears that the dianion precursor of 1-decanol decomposes to olefin very soon after its formation as expected from Barluenga's report.[9a]

The fact that *trans*- and *cis*-5-decene oxide produce only olefin (entries 9–11) when subjected to reductive lithiation is further confirmation of this concept. However, while cyclooctene oxide produces mainly olefin, a significant proportion of the product is cyclooctanol (entry 14). Even more striking is the fact that cyclohexene oxide yields three times more alcohol than alkene; Bartmann also reported a substantial yield of cyclohexanol from protonic quenching of the intermediate in the case of cyclohexene oxide.[2] The intermediate in this case can also be captured by an aldehyde (see below) and also by sulfenylation.[2] It seems likely that the stability of the lithium β-lithioalkoxide intermediate **11** is due to the fact that only one (**11d**) of the four chair conformers of **11** has the requisite steroelectronic arrangement for elimination and that conformer must be substantially less stable than the others due to 1,3-diaxial repulsions; it should be borne in mind that the lithium atoms must be heavily solvated and therefore occupy a great deal of volume. Of course, this is a simplified picture since the state of aggregation in unknown. The intermediate in the case of cyclooctene oxide must be more flexible than **11** but less so than those from the 5-decene oxides, thus accounting for its intermediate degree of stability toward elimination.



An explanation of the regiochemistry of Birch-type reductive cleavages of epoxides has been given in terms of a nucleophilic attack of solvated electrons on the carbon atom of the epoxide ring.[8b] This S_N2 type attack would be expected to result in predominant formation of the least substituted carbanion, as found, and it would also be consistent with the large rate decrease observed in going from 1,1-disubstituted to 1,2-disubstituted oxiranes (Table I). However, such a mechanism does not account well for the quantitative degree of attack at the unsubstituted as opposed to the substituted carbon atom of the epoxide ring. In the case of 1-decene oxide the ratio of attack at the least substituted to that at the most substituted carbon atom is about 2 whereas in a "typical" S_N2 reaction (of an alkyl halide), a single alkyl group at the α-position leads to a rate decrease by a factor of 40.[10] The corresponding ratio in entry 8, in which one of the carbon atoms carries two alkyl groups, is only 9 which appears to be orders of the magnitude too small. Furthermore, β-branching only results in a 2.5-fold increase in the ratio of attack at the least and most substituted carbon atoms (entries 3 and 7) whereas a typical rate decrease upon β-branching in an S_N2 reaction is by a factor of 12.[10] Finally, since an S_N2 type displacement by a solvated electron apparently does not have precedent, and since the epoxide radical anion, associated with a lithium ion, is found to be a minimum on the potential energy surface[11] for reductive lithiation of oxirane, we favor such an intermediate.

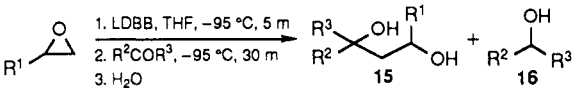
On this basis, the regiochemistry shown in eq 2 may appear surprising at first glance since the *least* substituted radical appears to be generated after cleavage of the radical anion which is produced when the epoxide absorbs an electron. A possible explanation of the cleavage of the intermediate radical anion **12** to produce the less branched radical **13** rather than its regioisomer (eq 3) has to do with



the energetic preference for the more branched carbinol derivatives and is treated in a separate publication.[11] The rate decrease in going from monosubstituted or 1,1-disubstituted oxiranes to 1,2-disubstituted oxiranes may be attributed to the greater steric hindrance toward association of the epoxide radical anion with the lithium ion in

(10) Streitwieser, A., Jr. *Solvolytic Displacement Reactions*; McGraw-Hill: New York, 1962; p 13.
(11) Dorigo, A. E.; Houk, K. N.; Cohen, T. *J. Am. Chem. Soc.*, submitted.

Table II. Reactions of the Reductive Lithiation Products of Ethylene and Propylene Oxides with Aldehydes and Ketones

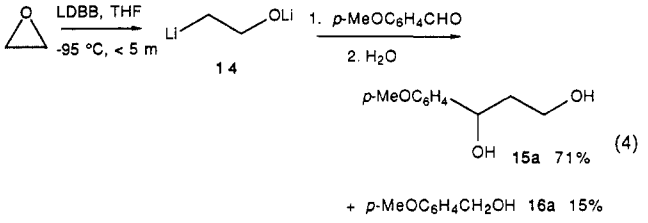


R¹	R²	R³	diol	% yield 15	% yield 16
H	*p*-$MeOC_6H_4$	H	**15a**	71	15
	Me_2CH		**15b**	55	*a*
	c-C_6H_{11}		**15c**	58	19
	CH_2=CH		**15d**	40	*a*
	n-C_6H_{13}		**15e**	51	~15
			**15f**	64	*a*
			**15g**	74	<10
	Me_2C=CH	Me	**15h**	44	*a*
			**15i**	44	16
	$-(CH_2)_5-$		**15j**	45	~20
	$-(CH_2)_3CH$=CH-		**15k**	51	<10
Me	*p*-$MeOC_6H_4$	H	**15l**	65[b]	12
			**15m**	52[b]	~13
		Me	**15n**	53	~10

[a] Yield of **16** not determined. [b] Two diastereomers.

the latter case in which neither side of the epoxide ring is free of substituents. Ethylene oxide itself is the most rapidly reduced of any saturated epoxide that we have studied (see below).

2. Reactions of Lithium β-Lithioalkoxides with Aldehydes and Ketones. A great deal of effort was expended to find optimum conditions for generation of the heretofore unkown parent, lithium 2-lithioethoxide (**14**) and for its reaction with *p*-anisaldehyde (eq 4). A major



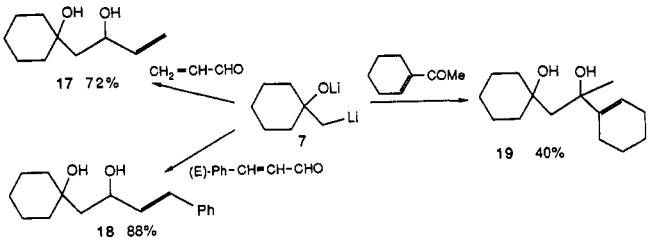
(4)

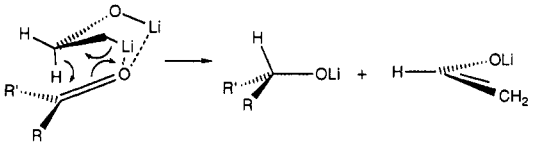
byproduct was *p*-methoxybenzyl alcohol, apparently resulting from hydride transfer from the dianion **14** to the aldehyde; the radical anion LDBB reductively dimerizes the aldehyde to a glycol instead of resulting in *p*-methoxybenzyl alcohol (**16a**). The ratio of diol **15a** to alcohol was substantially greater at −95 °C than at −78 °C. The yields shown in eq 4 are based on aldehyde; a 2-fold excess of epoxide and LDBB was employed. Under similar conditions, other aldehydes and ketones reacted with **14** to give moderate yields of glycols accompanied by alcohols (the yields of which ranged from less than 10% to 20%); these reactions are summarized in Table II.

Propylene oxide opened mainly to produce the branched alcohol. The proximate reduction product behaved with aldehydes and ketones much like its unsubstituted analogue **14**. The major products arose from addition to the carbonyl group and minor amounts of alcohols were also produced. These results are summarized in the last three entries of Table II.

Organometallics, particularly Grignard reagents, bearing β-hydrogen atoms frequently transfer hydride ions to carbonyl groups[12] and metallic salts of primary and secondary alcohols likewise behave as hydride ion donors[13] (the best known reaction of this type is the Meerwein–Pondorf–Verley reduction). Thus, it is not surprising that molecules such at **14** which possess both of these features can behave as hydride ion donors.[14] Molecular models indicate that both lithium atoms of **14** may be able to coordinate with the oxygen atom of the carbonyl group during the transfer as shown in eq 5.

Scheme I



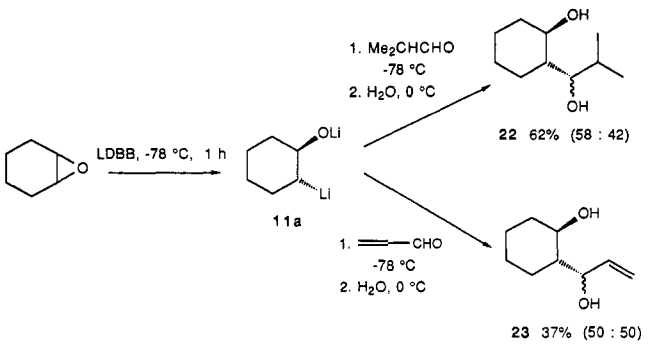


(5)

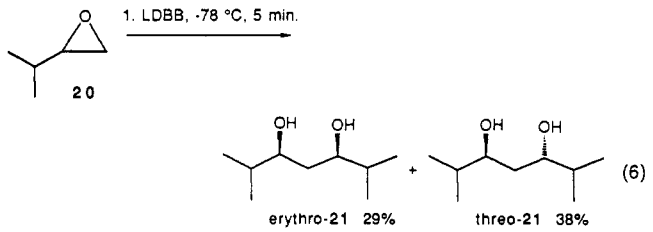
Of course, the lithium β-lithioalkoxide **7**, derived from the spiroepoxide **4** is incapable of transferring a hydride ion and its additions to aldehydes proceed in better yields. Examples are shown in Scheme I; also shown in that scheme is an addition to a conjugated enone in which steric crowding may lead to enolate formation via deprotonation of the exposed methyl group, thus somewhat reducing the yield of 1,2-adduct.

(12) March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley & Sons: New York, 1985; p 822.
(13) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 2nd ed.; Plenum Press: New York, 1983; Part B, pp 218–219.
(14) An analogy is the hydride ion transfer to an aldehyde carbonyl group from the dianion of an aldehyde hydrate which occurs during the Cannizzaro reaction.[13]

Scheme II

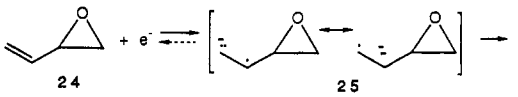


Attempts to control diastereoselectivity in the reaction of the reductive cleavage product of isopropyloxirane (**20**) with isobutyraldehyde proved futile. The relative yields of erythro and threo diols **21** shown in eq 6 underwent only minor changes upon addition of the complexing salts magnesium chloride, cerium chloride, dimethylaluminum chloride, and titanium tetraisopropoxide as well as tetramethylethylenediamine, a complexing agent for lithium ions. Furthermore, the metal salts all sharply lowered the yields of glycol; the sensitivity of the β-lithioalkoxides to destruction by complexing metals is quite general and is presumably attributable to catalysis of the olefin-forming elimination. The stereochemistry of the glycols was easily determined by NMR analysis of their acetone acetals.[15]



Reductive lithiation of cyclohexene oxide apparently leads largely to **11a** since subsequent capture by aldehydes leads to trans-2-substituted cyclohexanols (Scheme II; numbers in parentheses represent ratios of the two trans diastereomers that were produced). However, **11a** may be in equilibrium with the cis isomer since Bartmann found that trapping with deuterons led to cis product as well.[2]

Reductive lithiation of vinyloxirane **24**, the monoepoxidation product of 1,3-butadiene, was more facile than any other epoxide studied (Table III), and it resulted in production of the *less substituted* alcoholate anion as well as an allylic carbanion. The facility of the reduction allowed it to occur at −95 °C for short times. These conditions provided higher yields than reductions at −78 °C presumably due to slower destruction of the dianion which is produced. The reversal in regiochemistry is not unexpected as Bartmann had observed the analogous direction of opening in the case of styrene oxide.[2] In the case of **24** the greatly increased stability of the allylic radical intermediate outweighs the decreased stability of the primary alcoholate anion. The increased rate of reaction may also be attributed to the stability of this allylic radical as reflected in the transition state for its formation. However, a different explanation for both the regiochemistry and rate is also possible. The electron may find a lower energy home in the antibonding π orbital than in an antibonding σ CO bond orbital. This would increase either the rate of production of the radical anion **25** (if it is produced irreversibly) or its equilibrium concentration (if it is produced in an equilibrium prior to the ring-opening rate-determining step); in either case, a rate increase over the reduction of saturated epoxides could result. Furthermore, this concept also accounts for the regiochemistry, for the radical anion **25** can only cause ring fragmentation in the direction observed (eq 7).



$CH_2{=}CH{=}CH{-}CH_2O^-$ (7)

Treatment of the reductive cleavage product of vinyl oxirane with isobutyraldehyde produced *anti*- and *syn*-**26**, the products of carbonyl addition to the most substituted terminus of the allylic anion, as well as *trans*- and *cis*-**27**, the product of carbonyl addition to the least substituted allylic terminus (Table III). The yields were in the 50% range, and, as usual with reactions of all allyllithiums with carbonyl compounds,[16] regio- and stereoselectivities were low. As has been observed in the reactions of other allylic anions,[16] the addition of titanium tetraisopropoxide provided products derived mainly from attack on the most substituted terminus. The titanium(IV) reagent also greatly enhanced the stereoselectivity leading very largely to *anti*-**26**. These improvements in selectivity are completely in accord with the affect of this reagent in the cases of simpler allylic anions[5,16] and are explicable on the basis of Zimmerman–Traxler type chair transition state **29** proceeding from an organotitanium compound **28** in which the metal, with its large ligands, is attached to the least crowded allylic terminus. It is assumed that the allyltitanium, like similarly σ-bonded allyl Grignard reagents, is mainly trans.

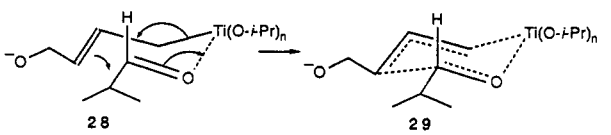
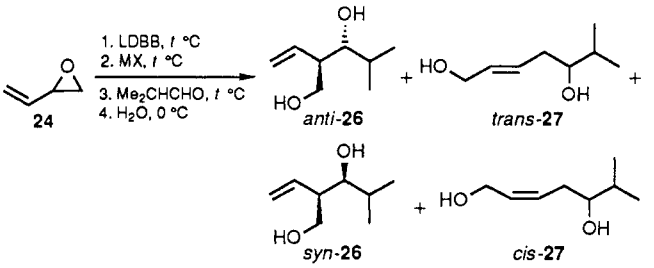


Table III. Reactions of the Reductive Lithiation Product of Vinyloxirane with Isobutyraldehyde



time, min	temp, °C	salt, MX	isolated yields, % 26 (anti:syn)[a]	27 (trans:cis)[b]
1	−78	–	28 (34:66)	18 (52:48)
5	−78	–	28 (34:66)	20 (48:52)
5	−78	$Ti(i\text{-}PrO)_4$[c]	24 (>95:<5)	3 (55:45)
1	−95	–	37 (40:60)	18 (87:13)
1	−95	$Ti(i\text{-}PrO)_4$[c]	35 (88:12)	3 (47:53)
1	−95	$CeCl_3$[d]	10 (37:63)	24 (88:12)
1	−95	$CeCl_3$[c]	32 (33:67)	12 (64:36)

[a] Anti:syn ratio obtained by NMR. [b] Trans:cis ratio obtained by chromatographic separation. [c] 2 equiv. [d] 1 equiv.

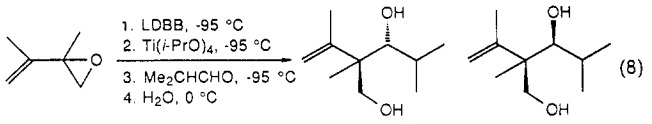
(15) Beckwith, A. L. J.; Wagner, R. D. *J. Am. Chem. Soc.* **1979**, *101*, 7099.

(16) (a) Cohen, T.; Guo, B.-S. *Tetrahedron* **1986**, *42*, 2803 and citations therein; (b) Guo, B. S.; Doubleday, W.; Cohen, T. *J. Am. Chem. Soc.* **1987**, *109*, 4710 and citations therein.

It was recently discovered in this laboratory that the addition of $CeCl_3$ to hydrocarbon allyl anions directs an attacking carbonyl group to the least substituted terminus, presumably because the metal forms a π rather than a σ bond.[5,16b] Cerium(III) chloride has the same effect in the present system although only when 1 molar equiv is used. The reason for the reversal of regiochemistry when 2 molar equiv are used is not obvious. Hydrocarbon allyllithiums with a terminal alkyl substituent exist largely in this cis configuration and can be captured by cerium(III) chloride to yield mainly cis adducts with aldehydes.[16b] The predominant production of trans adducts in the present case is quite understandable on the basis of the expected electrostatic repulsion between the partially negative allylic terminus and the oxyanionic substituent.

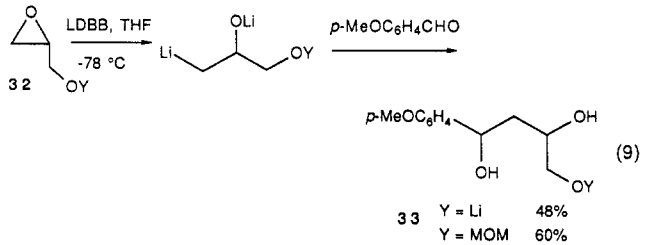
Unfortunately, the addition of the two salts which so increase selectivity decrease the yields. However, the selective production of reasonably complex molecules in a one-pot reaction from commercial reagents should be of synthetic use.

The monoepoxide **30** of 2,3-dimethyl-1,3-butadiene underwent reductive lithiation followed by sequential treatment with titanium tetraisopropoxide and isobutyraldehyde to provide very largely one glycol (eq 8). It is assumed on the basis of the above analogy that this product has the anti configuration (*anti*-**31**). Only a trace of product arising from attack of the aldehyde at the least substituted terminus was formed.



(8)

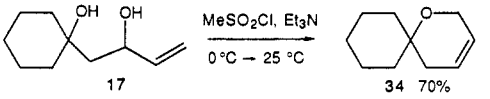
One of the attractions of the use of β-lithioalkoxides formed from epoxides is that optically active versions should be readily available by reductive lithiation of epoxides generated by Sharpless oxidation of allylic alcohols.[17] In order to test the ability to perform such reductive lithiations, glycidol (**32**; Y = H) was subjected to the usual conditions after protection of the hydroxyl group as (1) the lithium salt and (2) the methoxymethyl (MOM) ether (eq 9). The lithium salt reacted very sluggishly but,



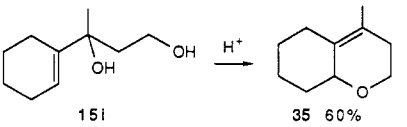
(9)

after several hours, 48% of the adduct **33** (Y = Li; isolated as the alcohol) was produced provided that a 2-fold excess of the epoxide and reducing agent was used; when the reagents were used in equimolar quantities, the yield was only 27%. As expected, the MOM ether reacted very rapidly, and the yield of adduct **33** (Y = MOM) was moderate.

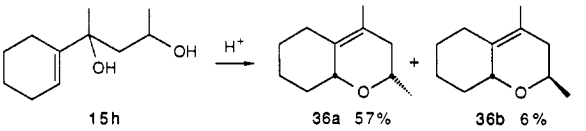
A potentially valuable synthetic use of this chemistry is the cyclization of the reaction products of the β-lithioalkoxides with conjugated enones to produce cyclic unsaturated ethers. This cyclization could be accomplished in one pot by activating the allylic hydroxyl group toward displacement by the other hydroxyl group with allylic inversion. Examples are shown in eqs 10–13.



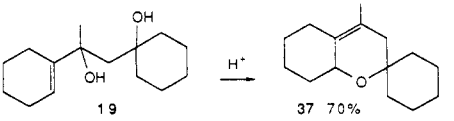
(10)



(11)



(12)



(13)

Conclusions

Given the wide availability of epoxides and the ease of the procedure, reductive lithiation of epoxides appears to be the most general method of generation of β-lithioalkoxides. These species have been prepared previously by somewhat more laborious paths from less readily available reagents. These methods include deprotonation of β-hydroxymercurials followed by mercury–lithium exchange[18] and deprotonation of β-chlorohydrins followed by reductive lithiation with lithium naphthalenide.[9] Although this latter method has been applied to the preparation of chiral β-lithioalkoxides by Nájera, Yus, and Seebach,[9c] the ease with which individual enantiomers of epoxides can be prepared will probably make reductive lithiation of epoxides the method of choice for this task. A large variety of these dianions have now been prepared by this procedure and their reactions with aldehydes and ketones provide useful polyols, sometimes with considerable stereocontrol. When the carbonyl partner is a conjugated enal or enone, the polyols can usually be cyclized to unsaturated cyclic ethers. The widespread availability of enantiomerically enriched or pure epoxides,[17] which in most cases will reductively cleave to optically active dianions, should greatly increase the synthetic utility of this methodology.

Experimental Section

General Methods. Reductive lithiations were carried out under an atmosphere of prepurified argon. Solvents were dried by the standard procedures and distilled before use. The cold bath temperatures were obtained using ice–water (0 °C), dry ice–isopropyl alcohol (−78 °C), or a Model TC-10 Flexi Cool cold probe (below −78 °C). Melting points are uncorrected. Infrared spectra were recorded on an IR/32 FTIR spectrometer. ^1H NMR spectra were obtained in deuteriochloroform on a Brucker AF 300 or Brucker AM 500 NMR spectrometer. Chemical shifts are reported in units of δ (ppm) relative to tetramethylsilane as an internal standard. High-resolution mass spectra were recorded on a CH-5 double-focusing Varian Mat mass spectrometer or on a VG 70G mass spectrometer. Radial chromatography was performed on a Harrison chromatotron using Merck silica gel 60 PF_{254}. Medium-pressure liquid chromatography was performed on a prepacked EM Lobar Lichoprep Si 60 column (40–63 μm, Merck). Thin-layer chromatography was performed on glass supported 250-μm silica gel GF plates (Analtech). For TLC

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detection, 254-nm UV lamps and a spray of 7% polyphosphomolybdic acid in 95% ethanol were used. Gas–liquid chromatography was performed on a Hewlett-Packard 5890 gas chromatograph equipped with a capillary column (Carbowax 20M) and a flame ionization detector, helium being used as a carrier gas.

Starting Materials. All carbonyl compounds were commercial reagents of the highest grade (Aldrich) and were purified by distillation immediately before use. 1-Oxaspiro[2.5]octane (**4**), cyclohexyloxirane (**8**; R^1 = c-C_6H_{11}, R^2 = R^3 = H), 1,2-epoxy-3-methylbutane (**20**), and 1,2-epoxy-2,3-dimethyl-3-butene (**30**) were prepared by the *m*-chloroperoxybenzoic acid oxidation of the corresponding olefins in methylene chloride at 0 °C.[19] Ethylene oxide was used as a 3.38 M solution in tetrahydrofuran (its concentration was determined and occasionally checked by ^{1}H NMR) and was stored under argon at −20 °C. The other epoxides were commercial samples and were purified by distillation before use.

2-(Phenylthio)-1-oxaspiro[2.5]octane (1).[20] To a solution of thioanisole (2.36 mL, 20 mmol) in THF (30 mL) was added dropwise *n*-butyllithium (13.1 mL of 1.6 M solution in hexane, 21 mmol) at 0 °C. After the reaction mixture had warmed to room temperature, stirring was continued for 20 h. It was cooled again to −78 °C, and cyclohexanone (2.08 mL, 20 mmol) was added dropwise. After 1 h, the mixture was allowed to warm to room temperature, stirred for 1 more hour, and quenched with water. Ether extraction and solvent evaporation furnished crude 1-((phenylthio)methyl)cyclohexanol, which was purified by radial chromatography (81% yield). A solution of 1-((phenylthio)-methyl)cyclohexanol (1.8 g, 8.1 mmol) and *N*-chlorosuccinimide (1.1 g, 8.4 mmol) in dry carbon tetrachloride (150 mL) was stirred at 0 °C for 24 h. The mixture was filtered and after solvent removal 2.0 g of the crude 1-[(phenylthio)chloromethyl]cyclohexanol was obtained: IR (neat) 3496, 3043, 2964, 2870, 1590, 1490, 1456 cm^{-1}; ^{1}H NMR δ 1.56–1.94 (m, 10 H), 2.05 (br s, 1 H), 5.23 (s, 1 H), 7.33–7.57 (m, 5 H); exact mass calcd for $C_{13}H_{17}OClS$ (M^+) 256.0690, found 256.0690. The α-chloro sulfide (12.5 g, 48.6 mmol) in THF (500 mL) at 0 °C was treated with *n*-butyllithium (32.2 mL of 1.51 M solution in hexane) by dropwise addition of the latter. After being stirred for 1 h, the solution was allowed to warm to room temperature, the solvent was evaporated, hexane was added, and precipitated LiCl was removed by filtration. Solvent evaporation and flash chromatography gave 7.5 g (70%) of pure 2-(phenylthio)-1-oxaspiro[2.5]octane (**1**): IR (neat) 3059, 2856, 1583, 1480, 1440, 1025 cm^{-1}; ^{1}H NMR δ 1.54–1.85 (m, 10 H), 4.28 (s, 1 H), 7.25–7.52 (m, 5 H); exact mass calcd for $C_{13}H_{16}OS$ (M^+) 220.0922, found 220.0922.

Preparation of Lithium 4,4′-Di-*tert*-butylbiphenylide (LDBB).[6] Several pieces of lithium metal (32 mg, 4.5 g-atoms) were added under an argon purge to an oven-dried 50-mL three-necked round-bottomed flask equipped with a glass stirring bar, argon inlet, and low-scale thermometer and containing 1.1 g (4.1 mmol) of DBB in 10 mL of dry THF. Prior to its addition, the lithium was scraped under pentane to remove any oxide and nitride from its surface. The mixture was then cooled to 0 °C, and the dark blue-greenish color of the radical anion solution appeared within 1–5 min. After 4 h of vigorous stirring at 0 °C, all the lithium had reacted. The resulting 0.4 M solution of LDBB in THF was used in reactions with epoxides.

Reductive Lithiation of 2-(Phenylthio)-1-oxaspiro[2.5]-octane (1). Deuteration and Methylation of the Intermediate β-Lithioalkoxide. To a preformed solution of LDBB (2.1 mmol) in THF (5 mL) at −78 °C was added dropwise **1** (220 mg, 1 mmol) in THF (5 mL). The mixture immediately changed color from dark blue-green to deep red. The resulting β-lithioalkoxide was quenched at −78 °C with CH_3OD or freshly distilled MeI (0.13 mL, 2 mmol). After the mixture had been warmed to room temperature, water was added and the organic material was extracted with ether (2 × 20 mL). The organic layer was dried over anhydrous $MgSO_4$, and the solvents were removed by rotary evaporation. Products **2** and **3** were isolated by flash chromatography. 1-[(Phenylthio)deuteriomethyl]cyclohexanol (**2**) (0.14 g, 63%): IR (neat) 3422, 3057, 2932, 2856, 1583, 1479, 1439 cm^{-1}; ^{1}H NMR δ 1.22–1.68 (m, 10 H), 2.1 (br s, 1 H), 3.09 (t, J = 1.5 Hz, 1 H), 7.15–7.43 (m, 5 H); exact mass calcd for $C_{13}H_{17}DOS$ (M^+) 223.1141, found 223.1142. 1-(1-(Phenylthio)ethyl)cyclohexanol (**3**)[21] (0.10 g, 42%): ^{1}H NMR δ 1.37 (d, J = 6 Hz, 3 H), 1.5–1.7 (m, 10 H), 2.17 (br s, 1 H), 3.22 (q, J = 6 Hz, 1 H), 7.1–7.5 (m, 5 H).

Reductive Cleavage of Epoxides 8. Determination of the Alcohol:Olefin Ratio after Protonation of the Intermediate β-Lithioalkoxides. Epoxides **8** (1 mmol) were added dropwise to a preformed solution of LDBB (2.1 mmol) in THF (5 mL) at −78 °C. After a designated time the reaction was quenched with methanol (1 mL) at −78 °C, and the mixture was warmed to 0 °C and then diluted with water (15 mL). The organic material was extracted with ether (2 × 20 mL), and the combined organic layer was dried over anhydrous $MgSO_4$. The alcohols **9** and the olefins **10**, derived from the corresponding epoxides **8**, were identified by comparing their retention times with those of the authentic samples chromatographed under identical conditions. The relative ratios of the components were established as average values taken from the integration of the corresponding peaks from several injections.

Reductive Cleavage of Ethylene Oxide and Propylene Oxide. Synthesis of 1,3-Diols 15. A Typical Procedure. Ethylene oxide (0.60 mL of 3.38 M solution in THF, 2 mmol) or propylene oxide (116 mg, 2 mmol) was added dropwise to a preformed solution of LDBB (4.1 mmol) in THF (15 mL) at −95 °C. A 5–10 °C increase in temperature was observed. After it had been stirred for a few minutes, the resulting deep red solution was treated with aldehydes or ketones (1 mmol for ethylene oxide; 2 mmol for propylene oxide). The dark red color turned to a light yellow after 5–30 min of stirring at −95 °C. After the mixture had been warmed to 0 °C, water (5 mL) was added, and the organic material was extracted with ether (3 × 20 mL). The combined ether layer was dried with anhydrous $MgSO_4$, and the solvent was removed by rotary evaporation. The products were isolated by radial chromatography (hexane/ethyl acetate, 1:1). The known alcohols **16** were identified by comparing their ^{1}H NMR spectra and TLC R_f values with those of authentic samples. The spectral data of the diols **15** are as follows. **1-(4-Methoxyphenyl)-1,3-propanediol (15a)**:[22] IR (neat) 3394, 2950, 2838, 1613, 1586, 1514, 1248, 1035 cm^{-1}; ^{1}H NMR δ 1.9 (m, 2 H), 3.13 (br s, 1 H), 3.45 (br s, 1 H) 3.78 (s, 3 H), 4.84 (dd, J = 3.8 and 8.7 Hz, 1 H), 6.86 (d, J = 8.7 Hz, 2 H), 7.25 (d, J = 8.7 Hz, 2 H); exact mass calcd for $C_{10}H_{14}O_3$ 182.0943 (M^+), found 182.0943. **4-Methyl-1,3-pentanediol (15b)**:[23] IR (neat) 3355, 2966, 1480, 1068 cm^{-1}; ^{1}H NMR δ 0.90 (d, J = 5.6 Hz, 3 H), 0.92 (d, J = 5.6 Hz, 3 H), 1.68 (m, 3 H), 2.76 (br s, 1 H), 2.91 (br s, 1 H), 3.60 (m, 1 H), 3.85 (m, 2 H); exact mass calcd for $C_6H_{12}O$ (M^+ − 18) 100.0888, found 100.0888. **1-Cyclohexyl-1,3-propanediol (15c)**:[24] IR (neat) 3350, 2925, 2855, 1703, 1455, 1070 cm^{-1}; ^{1}H NMR δ 0.9–1.4 (m, 6 H), 1.6–1.9 (m, 7 H), 2.69 (br s, 2 H), 3.59 (m, 1 H), 3.84 (m, 2 H); exact mass calcd for $C_9H_{17}O$ (M^+ − 17) 141.1279, found 141.1279. **4-Pentene-1,3-diol (15d)**:[25] IR (neat) 3340, 2945, 2885, 1654, 1425, 1065 cm^{-1}; ^{1}H NMR δ 1.77 (m, 2 H), 2.96 (br s, 1 H), 3.08 (br s, 1 H), 3.81 (m, 2 H), 4.36 (m, 1 H), 5.12 (dt, J = 1.3 and 10.4 Hz, 1 H), 5.26 (dt, J = 1.3 and 17.3 Hz, 1 H), 5.89 (ddd, J = 5.8, 10.4, and 17.3 Hz, 1 H); exact mass calcd for $C_5H_9O_2$ (M^+ − 1) 101.0602, found 101.0602. **1,3-Nonanediol (15e)**:[26] IR (neat) 3345, 2933, 2870, 1465, 1060 cm^{-1}; ^{1}H NMR δ 0.87 (m, 3 H), 1.2–1.6 (m, 2 H), 2.76 (br s, 2 H), 3.85 (m, 3 H); exact mass calcd for $C_9H_{20}O_2$ (M^+) 160.1463, found 160.1463. **(*E*)-4-Hexene-1,3-diol (15f)**:[27] IR (neat) 3358, 2940, 2884, 1679, 1440, 1057,

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966 cm^{-1}; ^{1}H NMR δ 1.69 (d, J = 6.0 Hz, 3 H), 1.74 (q, J = 5.8 Hz, 2 H), 2.81 (br s, 1 H), 2.92 (br s, 1 H), 3.79 (m, 2 H), 4.30 (br q, 1 H), 5.51 (ddd, J = 1.2, 6.7, and 15.3 Hz, 1 H), 5.68 (dq, J = 6.0 and 15.3 Hz, 1 H); exact mass calcd for $C_6H_{12}O_2$ (M^+) 116.0837, found 116.0837. **(*E*)-5-Phenyl-4-pentene-1,3-diol (15g)**:[28] mp 71–72 °C; IR (neat) 3308, 3023, 2953, 1452, 1217, 1066, 966, 754 cm^{-1}; ^{1}H NMR δ 1.87 (m, 2 H), 2.89 (br s, 1 H), 3.14 (br s, 1 H), 3.86 (m, 2 H), 4.55 (br q, J = 6.1 Hz, 1 H), 6.24 (dd, J = 6.5 and 15.9 Hz, 1 H), 6.60 (d, J = 15.9 Hz, 1 H), 7.2–7.4 (m, 5 H); exact mass calcd for $C_{11}H_{14}O_2$ (M^+) 178.0994, found 178.0994. **3,5-Dimethyl-4-hexene-1,3-diol (15h)**:[24] IR (neat) 3370, 2980, 2930, 1680, 1462, 1378, 1060 cm^{-1}; ^{1}H NMR δ 1.36 (s, 3 H), 1.71 (d, J = 1.2 Hz, 3 H), 1.82 (m) and 1.83 (d, J = 1.1 Hz) (5 H), 2.64 (br s, 1 H), 2.83 (br s, 1 H), 3.85 (m, 2 H), 5.24 (m, 1 H); exact mass calcd for $C_8H_{16}O_2$ (M^+) 144.1150, found 144.1152. **3-(Cyclohexen-1-yl)-1,3-butanediol (15i)**: IR (neat) 3385, 2945, 1705, 1670, 1458 cm^{-1}; ^{1}H NMR δ 1.29 (s, 3 H), 1.4–2.1 (m, 10 H), 2.70 (br s, 1 H), 2.81 (br s, 1 H), 3.73 (br t, J = 5.3 Hz, 2 H), 5.83 (m, 1 H); exact mass calcd for $C_{10}H_{18}O_2$ (M^+) 170.1307, found 170.1306. **1-(2-Hydroxyethyl)cyclohexanol (15j)**:[29] IR (neat) 3360, 2940, 2866, 1462, 1068 cm^{-1}; ^{1}H NMR δ 1.2–1.7 (m, 10 H), 1.71 (t, J = 5.7 Hz, 2 H), 2.70 (br s, 1 H), 3.16 (br s, 1 H), 3.86 (m, 2 H); exact mass calcd for $C_8H_{16}O_2$ (M^+) 144.1150, found 144.1152. **1-(2-Hydroxyethyl)-2-cyclohexen-1-ol (15k)**: IR (neat) 3365, 3023, 2933, 1702, 1435, 1085, 1055 cm^{-1}; ^{1}H NMR δ 1.5–2.1 (m, 8 H), 2.71 (br s, 1 H), 3.16 (br s, 1 H), 3.87 (m, 2 H), 5.70 (d, J = 10.1 Hz, 1 H), 5.79 (dt, J = 3.4 and 10.1 Hz, 1 H); exact mass calcd for $C_8H_{14}O_2$ (M^+) 142.0994, found 142.0994. **1-(4-Methoxyphenyl)-1,3-butanediol (15l)**: IR (neat) 3395, 2945, 2840, 1615, 1515, 1250, 1038 cm^{-1}; ^{1}H NMR (diastereomer ratio 53:47) (major) δ 1.19 (d, J = 6.0 Hz, 3 H), 1.65–1.9 (m, 2 H), 3.0 (br s, 2 H), 3.79 (s, 3 H), 4.05–4.15 (m, 1 H), 4.85 (dd, J = 3.0 and 10.0 Hz, 1 H), 6.86 (d, J = 8.5 Hz, 2 H), 7.26 (d, J = 8.5 Hz, 2 H); (minor) δ 1.22 (d, J = 6.2 Hz, 3 H), 1.84 (m, 2 H), 3.0 (br s, 2 H), 3.79 (s, 3 H), 4.05 (m, 1 H), 4.98 (dd, J = 3.7 and 7.9 Hz, 1 H), 6.87 (d, J = 8.7 Hz, 2 H), 7.27 (d, J = 8.7 Hz, 2 H); exact mass calcd for $C_{11}H_{16}O_3$ (M^+) 196.1099, found 196.1098. **(*E*)-6-Phenyl-5-hexene-2,4-diol (15m)**: IR (neat) 3371, 3027, 2969, 2932, 1703, 1599, 1416 cm^{-1}; ^{1}H NMR (diastereomer ratio 53:47) δ 1.23 (d, J = 5.4 Hz) and 1.25 (d, J = 5.6 Hz) (3 H), 1.65–1.8 (m, 2 H), 3.2 (br s, 2 H), 4.05–4.25 (m, 1 H), 4.54 (br q, J = 6.5 Hz) and 4.64 (br q, J = 5.4 Hz) (1 H), 6.21 (dd, J = 6.5 and 15.9 Hz) and 6.28 (dd, J = 5.4 and 15.9 Hz) (1 H), 6.59 (d, J = 15.9 Hz) and 6.63 (d, J = 15.9 Hz) (1 H), 7.2–7.4 (m, 5 H); exact mass calcd for $C_{12}H_{16}O_2$ (M^+) 192.1150, found 192.1149. **2-(Cyclohexen-1-yl)-2,4-pentanediol (15n)**: IR (neat) 3384, 2968, 2933, 1705, 1651, 1455, 1373 cm^{-1}; ^{1}H NMR (diastereomer ratio 56:44) δ 1.13 (d, J = 6.3 Hz) and 1.16 (d, J = 6.3 Hz) (3 H), 1.24 (s) and 1.34 (s) (3 H), 1.4–2.1 (m, 10 H), 2.61 (br s) and 3.61 (br s) (1 H), 3.23 (br s, 1 H), 3.88 (m) and 4.17 (m) (1 H), 5.77 (m) and 5.85 (m) (1 H); exact mass calcd for $C_{10}H_{17}O_2$ (M^+ – 15) 169.1229, found 169.1229.

Reductive Cleavage of 1-Oxaspiro[2.5]octane and Reactions of the β-Lithioalkoxide (7) with Carbonyl Compounds. 1-Oxaspiro[2.5]octane (228 mg, 2 mmol) was added dropwise to a preformed LDBB (4.1 mmol) solution in THF (15 mL) at –78 °C. After a few minutes, a deep red color appeared, and the carbonyl compound (neat or as a THF solution, 2 mmol) was added. The mixture was stirred for 30 min and warmed to 0 °C, and the reaction was quenched with water (5 mL) and worked up as described in the previous procedure. Products **17–19** were isolated by radial chromatography (20–35% ethyl acetate in hexane).

1-(2-Hydroxy-3-butenyl)cyclohexanol (17): IR (neat) 3339, 3035, 2932, 2859, 1646, 1449, 1329, 1269, 1088 cm^{-1}; ^{1}H NMR δ 1.2–1.4 (m, 1 H), 1.44–1.67 (m, 10 H), 1.71–1.79 (m, 1 H), 3.0 (br s, 2 H), 4.52 (m, 1 H), 5.09 (d, J = 10.3 Hz, 1 H), 5.26 (d, J = 17.3 Hz, 1 H), 5.87 (ddd, J = 5.9, 10.3, and 17.3 Hz, 1 H); exact mass calcd for $C_{10}H_{18}O_2$ (M^+) 170.1307, found 170.1306. **1-(2-Hydroxy-4-phenyl-3-butenyl)cyclohexanol (18)**: mp 83–84 °C; IR (neat) 3295, 3025, 2932, 2857, 1705, 1600, 1500, 1455, 969, 754 cm^{-1}; ^{1}H NMR δ 1.3–1.85 (m, 12 H), 3.0 (br s, 1 H), 3.8 (br s, 1 H), 4.69 (m, 1 H), 6.21 (dd, J = 6.2 and 15.9 Hz, 1 H), 6.59 (d, J = 15.9 Hz, 1 H), 7.2–7.4 (m, 5 H); exact mass for $C_{16}H_{20}O$ (M^+ – 18) 228.1515, found 228.1514. **1-[2-(Cyclohexen-1-yl)-2-hydroxypropyl]cyclohexanol (19)**: IR (neat) 3350, 2980, 2932, 2870, 1670, 1458, 1095, 1060 cm^{-1}; ^{1}H NMR δ 1.26 (s, 3 H), 1.3–2.2 (m), 1.64 (d, J = 14.9 Hz) and 1.92 (d, J = 14.9 Hz) (20 H), 3.3 (br s, 2 H), 5.83 (m, 1 H); exact mass calcd for $C_{15}H_{24}O$ (M^+ – 18) 220.1827, found 220.1828.

Reductive Lithiation of 1,2-Epoxycyclohexane. Trapping the β-Lithioalkoxide 11a with Aldehydes. 1,2-Epoxycyclohexane (196 mg, 2 mmol) was added dropwise to a preformed LDBB (4.1 mmol) solution in THF (10 mL) at –78 °C. After the solution had been stirred for 1 h, acrolein (112 mg, 2 mmol) or isobutyraldehyde (144 mg, 2 mmol) was added. The mixture was stirred for 1 additional hour at –78 °C, warmed to 0 °C, and quenched with water (15 mL). A standard workup followed by radial chromatography yielded diastereomeric diols **20** and **21**. ***trans*-2-(1-Hydroxy-2-methylpropyl)cyclohexanol (20)**:[30] mp 104–105 °C; IR (neat) 3341, 2932, 2865, 1449, 1387, 1368, 1123, 990 cm^{-1}; ^{1}H NMR (diastereomer ratio 58:42) (major) δ 0.85 (d, J = 6.7 Hz, 3 H), 1.04 (d, J = 6.7 Hz, 3 H), 1.12–1.36 (m, 4 H), 1.63–2.07 (m, 8 H), 3.58 (dd, J = 2.1 and 9.4 Hz, 1 H), 3.64 (ddd, J = 4.4, 10.1, and 10.1 Hz, 1 H); (minor) δ 0.85 (d, J = 6.8 Hz, 3 H), 0.99 (d, J = 6.8 Hz, 3 H), 1.16–1.32 (m, 4 H), 1.57–2.05 (m, 8 H), 3.50 (dd, J = 2.2 and 9.2 Hz, 1 H), 3.56 (ddd, J = 4.2, 9.6, and 9.9 Hz, 1 H); exact mass calcd for $C_{10}H_{18}O$ (M^+ – 18) 154.1358, found 154.1357. ***trans*-2-(1-Hydroxy-2-propenyl)cyclohexanol (21)**: IR (neat) 3333, 3013, 2932, 2862, 1645, 1454, 1552, 1153, 993 cm^{-1}; ^{1}H NMR (diastereomer ratio 50:50) δ 1.1–1.8 (m, 8 H), 1.85–2.01 (m, 1 H), 3.14 (br s) and 3.27 (br s) (1 H), 3.60 (ddd, J = 4.1, 9.9, and 10.0 Hz, 1 H), 4.05 (t, J = 8.2 Hz), 4.12 (br s) and 4.24 (br s) (1 H), 5.17 and 5.23 (d, J = 10.2 Hz, 1 H), 5.22 and 5.31 (d, J = 17.3 Hz, 1 H), 5.84 and 6.00 (ddd, J = 6.0, 10.2, and 17.3 Hz, 1 H); exact mass calcd for $C_9H_{14}O$ (M^+ – 18) 138.1045, found 138.1045.

Reductive Lithiation of 3-Methyl-1,2-epoxybutane Followed by Treatment of the Intermediate β-Lithioalkoxide with Isobutyraldehyde. To a preformed solution of LDBB (4.7 mmol) in THF (12 mL) at –78 °C was added dropwide 3-methyl-1,2-epoxybutane (192 mg, 2.23 mmol). After the solution had been stirred for 5 min, isobutyraldehyde (214 mg, 2.97 mmol) was added. The mixture was stirred at –78 °C for 30 min and, after it had warmed to 0 °C, water (15 mL) was added. Following the standard workup, the two diastereomers (erythro:threo 43:57) of the diol **23** were isolated by radial chromatography (25% ethyl acetate in hexane). ***erythro*-2,6-Dimethyl-3,5-heptanediol (23)**[31] (100 mg, 29%): ^{1}H NMR δ 0.90 (d, J = 6.9 Hz, 12 H), 1.39 (dt, J = 10.2 and 14.4 Hz, 1 H), 1.57 (dt, J = 2.0 and 14.4 Hz, 1 H), 1.64–1.77 (m, 2 H), 3.14 (br s, 2 H), 3.63 (ddd, J = 2.0, 5.0, and 10.2 Hz, 1 H). ***threo*-2,6-Dimethyl-3,5-heptanediol (23)** (136 mg, 38%): mp 79–81 °C; ^{1}H NMR δ 0.91 (d, J = 6.9 Hz, 6 H), 0.96 (d, J = 6.9 Hz, 6 H), 1.60 (dd, J = 5.0 and 6.0 Hz, 2 H), 1.71 (m, 2 H), 2.12 (br s, 2 H), 3.65 (dt, J = 5.6 and 6.0, 2 H); IR (neat) 3355, 2961, 2876, 1468, 1385, 1368, 1152, 980 cm^{-1}; exact mass calcd for $C_9H_{18}O$ (M^+ – 18) 142.1358, found 142.1358. The stereochemical assignments for both diastereomers were confirmed by ^{1}H NMR spectra of their cyclic dimethyl acetals[15] prepared from **23** and 2,2-dimethoxypropane in the presence of a catalytic amount of *p*-toluenesulfonic acid in refluxing benzene using a Dean–Stark apparatus. The acetal derived from *erythro*-**23**, bearing two isopropyl groups in the axial and equatorial 4,6-positions of the 1,3-dioxane ring, showed a doublet of doublets of doublets at δ 3.45 ppm with the coupling constants J_{ea} = 2.3 Hz, $J_{a\text{-}iPr}$ = 6.7 Hz, and J_{aa} = 11.5 Hz. The corresponding H-4 and H-6 protons in the ^{1}H NMR spectrum of the *threo*-**23**-derived acetal exhibited a quartet at 3.37 ppm with J = 7.9 Hz.

Reductive Lithiation of 3,4-Epoxy-1-butene and 2,3-Dimethyl-3,4-epoxy-1-butene Followed by Treatment of the Intermediate Oxyallylic Anions with Isobutyraldehyde. 3,4-Epoxy-1-butene (70 mg, 1 mmol) or 2,3-dimethyl-3,4-epoxy-1-butene (98 mg, 1 mmol) was added dropwise to a preformed

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solution of LDBB (2.1 mmol) in THF (5 mL) at −95 °C. After 1 min, titanium isopropoxide (570 mg, 2 mmol) was added by a syringe or anhydrous cerium chloride (290 mg, 1.1 mmol), as a suspension in THF (3 mL), was cannulated to the dianion solution. The mixture was stirred for 30 min at −95 °C, and isobutyraldehyde (72 mg, 1 mmol) was then added. After 30 min of additional stirring and warming to 0 °C, the mixture was quenched with 5% hydrochloric acid (20 mL) and worked up in the standard way. Products **26** and **31** (as syn/anti mixtures), (*E*)-**27**, and (*Z*)-**27** were separated by radial chromatography (hexane/ethyl acetate, 1:1). **4-Hydroxy-3-(hydroxymethyl)-5-methyl-1-hexene (26)** (anti:syn 40:60 by ^{1}H NMR): IR (neat) 3357, 3075, 2959, 2874, 1638, 1472, 1385, 1053, 990 cm^{-1}; ^{1}H NMR δ 0.89 (d, J = 6.7 Hz), 0.97 and 0.99 (2 d, J = 6.6 Hz) (6 H), 1.68 (m) and 1.82 (m) (1 H), 2.3 (br s, 2 H), 3.42 (dd, J = 3.2 and 8.5 Hz) and 3.54 (dd, J = 3.3 and 8.2 Hz) (1 H), 3.70–3.86 (m, 2 H), 5.14–5.30 (m, 2 H), 5.63 (ddd, J = 9.0, 10.3, and 17.2 Hz) and 5.93 (ddd, J = 9.4, 10.5, and 17.3 Hz) (1 H); exact mass calcd for $C_8H_{14}O$ (M^+ − 18) 126.1045, found 126.1045. **(*E*)-6-Methyl-2-heptene-1,5-diol (27)**: ^{1}H NMR δ 0.94 and 0.95 (2 d, J = 6.8 Hz, 6 H), 1.69 (m, 1 H), 1.92 (br s, 2 H), 2.13 (m, 1 H), 2.29 (m, 1 H), 3.40 (m, 1 H), 4.12 (d, J = 4.0 Hz, 1 H), 5.74 (m, 2 H). **(*Z*)-6-Methyl-2-heptene-1,5-diol (27)**: ^{1}H NMR δ 0.94 and 0.95 (2 d, J = 6.8 Hz, 6 H), 1.70 (m, 1 H), 2.25 (m, 4 H), 3.38 (m, 1 H), 4.07 (dd, J = 6.7 and 12.2 Hz, 1 H), 4.22 (dd, J = 7.5 and 12.2 Hz, 1 H), 5.68 (m, 1 H), 5.87 (m, 1 H); irradiation of the two allylic protons at position 1 (δ 2.25, m) changed the multiplet at 5.68 (vinylic proton at position 2) into a doublet with J_{cis} = 10.0 Hz; IR (neat) 3335, 3080, 2959, 2872, 1671, 1468, 1385, 1090, 999 cm^{-1}; exact mass calcd for $C_8H_{14}O$ (M^+ − 18) 126.1045, found 126.1045. **4-Hydroxy-3-(hydroxymethyl)-2,3,5-trimethyl-1-hexene (31)** (anti:syn 93:7 by ^{1}H NMR): IR (neat) 3368, 3092, 2959, 2876, 1634, 1466, 1379, 1169, 974 cm^{-1}; ^{1}H NMR (anti) δ 0.96 and 0.97 (2 d, J = 6.7 Hz, 6 H), 1.10 (s, 3 H), 1.77 (s, 3 H), 1.82 (m, 1 H), 2.09 (br s, 2 H), 3.54 (d, J = 10.8 Hz, 1 H), 3.71 (d, J = 10.8 Hz, 1 H), 3.74 (d, J = 3.6 Hz, 1 H), 4.93 (s, 1 H), 5.01 (s, 1 H); (syn) δ 0.96 and 0.99 (2 d, J = 6.8 Hz, 6 H), 1.22 (s, 3 H), 1.80 (s, 3 H), 1.88 (m, 1 H), 1.99 (br s, 2 H), 3.49 (d, J = 2.8 Hz, 1 H), 3.68 (d, J = 10.6 Hz, 1 H), 3.87 (d, J = 10.6 Hz, 1 H). The structure of *anti*-**26** was confirmed by the ^{1}H NMR spectrum of its cyclic dimethyl acetal obtained in an analogous way to that described for diols **23**. The protons at position 6 absorbed at δ 4.13 (dd, J_{gem} = 11.4 Hz and J_{ee} = 1.8 Hz, H_{eq}) and 3.71 (dd, J_{gem} = 11.4 Hz and J_{ae} = 3.0 Hz, H_{ax}), respectively, and a proton at position 4 absorbed at δ 3.40 (dd, J_{ae} = 2.2 Hz and $J_{a\text{-}i\text{-}Pr}$ = 9.8 Hz, H_{ax}). From the splitting pattern indicating the cis arrangement of the isopropyl and vinyl substituents at positions 4 and 5, respectively, the structure of *anti*-**26** diol as the precursor of the produced acetal can be deduced.

Reductive Lithiation of Glycidol Lithium Salt and Methoxymethyl Ether. Trapping the Intermediate Tri- and Dianions with 4-Methoxybenzaldehyde. To a solution of glycidol (148 mg, 2 mmol) in THF was added dropwise under argon at −78 °C *n*-butyllithium (1.3 mL of 1.6 M solution in hexane). After 15 min, the alkoxide solution was cannulated to a preformed solution of LDBB (4.1 mmol) in THF (10 mL) at −78 to −70 °C. The mixture was stirred for 5 h, and 4-methoxybenzaldehyde (148 mg, 1.09 mmol) was injected into the mixture. After additional stirring for 30 min at −78 °C, weater (3 mL) was added. Ether workup followed by chromatotron isolation (3% MeOH in ethyl acetate) yielded 111 mg (48%) of 4-(4-methoxyphenyl)-1,2,4-butanetriol (**33**, Y = H): IR (neat) 3350, 2942, 2840, 1615, 1586, 1514, 1248, 1038, 833 cm^{-1}; ^{1}H NMR (anti:syn 50:50) δ 1.6–1.9 (m, 2 H), 3.45–3.65 (m, 3 H), 3.70 (s) and 3.75 (s) (3 H), 4.0 (m, 2 H), 4.18 (br s) and 4.36 (br s), (1 H), 4.83 (dd, J = 3.3 and 9.6 Hz) and 4.91 (m) (1 H), 6.82 and 6.83 (2 d, J = 8.6 Hz, 2 H), 7.21 and 7.23 (2 d, J = 8.6 Hz, 2 H); exact mass calcd for $C_{11}H_{16}O_4$ (M^+) 212.1049, found 212.1048.

Reductive lithiation of glycidyl methoxymethyl ether **32** (Y = $MeOCH_2$) (177 mg, 1.5 mmol) by LDBB (3.1 mmol) in THF (10 mL) required only 5 min under identical conditions. The intermediate β-lithioalkoxide was trapped with 4-methoxybenzaldehyde (192 mg, 1.4 mmol), yielding 216 mg (60%) of 4-(methoxymethoxy)-1-(4-methoxyphenyl)-1,3-butanediol (**33**, Y = $MeOCH_2$) after radial chromatography: IR (neat) 3360, 2975, 2950, 2915, 2840, 1615, 1515, 1250, 1045 cm^{-1}; ^{1}H NMR (anti:syn 50:50) δ 1.7–1.9 (m, 2 H), 3.12 (d, J = 4.3 Hz) and 3.19 (d, J = 3.8 Hz) (1 H), 3.34 and 3.35 (2 s, 3 H), 3.39–3.47 (m, 1 H), 3.51–3.60 (m, 1 H), 3.60 (br s, 1 H), 3.77 (s, 3 H), 3.98–4.06 (m, 1 H), 4.61 (s, 2 H), 4.89 (dd, J = 2.0 and 9.5 Hz) and 4.96 (dd, J = 5.5 and 10.3 Hz) (1 H), 6.85 (d, J = 8.8 Hz, 2 H), 7.26 and 7.27 (2 d, J = 8.8 Hz, 2 H); exact mass calcd for $C_{13}H_{20}O_5$ (M^+) 256.1311, found 256.1312.

Mesylation and Cyclization of 1-(2-Hydroxy-3-butenyl)-1-cyclohexanol (17). To a solution of **17** (48 mg, 0.28 mmol) and triethylamine (31 mg, 0.31 mmol) in methylene chloride (20 mL) was added at 0 °C methanesulfonyl chloride (33 mg, 0.29 mmol), and the mixture was stirred for 2 h at 0 °C and for 3 days at room temperature. After the mixture had been washed with 5% HCl and saturated $NaHCO_3$, the organic layer was dried over anhydrous Na_2CO_3 and the solvent was evaporated. Radial chromatography gave **34** (30 mg, 70%) along with the uncyclized mesylate ester of **17** (9 mg, 13%) as a minor product; 1-oxaspiro[5.5]undec-3-ene (**34**): ^{1}H NMR δ 1.25–1.62 (m, 10 H), 2.22 (d, J = 7.1 Hz, 2 H), 4.06 (d, J = 6.9 Hz, 2 H), 5.70 (m, 1 H), 5.87 (m, 1 H).

Cyclization of the Diols 15i, 15h, and 19 in the Presence of Acid. Diol **15i**, **15h**, or **19** (0.2 mmol) was stirred in methylene chloride (10 mL) with a catalytic amount of *p*-toluenesulfonic acid (5 mg) at room temperature for 5 min, 1 h, and 3 h, respectively. The mixture was washed with 5% $NaHCO_3$ solution (5 mL) and dried over anhydrous $MgSO_4$, and the solvent was evaporated. The cyclic products were obtained by radial chromatography (3–5% ethyl acetate in hexane). **4-Methyl-3,5,6,7,8,8a-hexahydro-2*H*-1-benzopyran (35)**:[32] IR (neat) 2950, 1720, 1458, 1380, 1100 cm^{-1}; ^{1}H NMR δ 1.05–1.50 (m, 4 H), 1.5–1.8 (m) and 1.65 (s) (6 H), 2.0 (m, 1 H), 2.3 (m, 1 H), 2.7 (m, 1 H), 3.57 (td, J = 3.5 and 10.7 Hz, 1 H), 3.90 (m, 1 H); exact mass calcd for $C_{10}H_{16}O$ (M^+) 152.1201, found 152.1202. **2,4-Dimethyl-3,5,6,7,8,8a-hexahydro-2*H*-1-benzopyran (36ab)**: IR (neat) 2975, 2866, 1737, 1467, 1385, 1105 cm^{-1}; ^{1}H NMR (diastereomer ratio 91:9) δ 1.11 (m, 1 H), 1.17 and 1.22 (2 d, J = 6.0 Hz) (3 H), 1.4–1.75 (m), 1.55 and 1.63 (2 s) (8 H), 1.75–2.1 (m, 4 H), 2.68 (m, 1 H), 3.60 (m) and 3.83 (m) (1 H), 3.93 (m, 1 H); exact mass calcd for $C_{11}H_{18}O$ (M^+) 166.1358, found 166.1358. **4′-Methyl-3′,5′,6′,7′,8′,8′a-hexahydrospiro[cyclohexane-1,2′-[2*H*]benzo-[*b*]pyran] (37)**: IR (neat) 2932, 2857, 1703, 1448, 1105 cm^{-1}; ^{1}H NMR δ 1.1–1.8 (m, 17 H), 1.61 (s, 3 H), 1.9–2.05 (m, 2 H), 2.67 (dd, J = 1.9 and 14.2), 3.78 (m, 1 H); exact mass calcd for $C_{15}H_{24}O$ (M^+) 220.1827, found 220.1827.

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78-83-1; **16c**, 100-49-2; **16d**, 107-18-6; **16e**, 111-70-6; **16f**, 504-61-0; **16g**, 4407-36-7; **16h**, 4325-82-0; **16i**, 18325-75-2; **16k**, 822-67-3; **17**, 124781-46-0; **18**, 124781-47-1; **19**, 124781-48-2; **20**, 1438-14-8; *erythro*-**21**, 65534-62-5; *threo*-**21**, 36471-61-1; *erythro*-**21** (acetonide), 124781-54-0; *threo*-**21** (acetonide), 124781-55-1; **22** (isomer 1), 108647-08-1; **22** (isomer 2), 124916-15-0; **23** (isomer 1), 124781-49-3; **23** (isomer 2), 124916-16-1; **24**, 930-22-3; *anti*-**26**, 122592-64-7; *syn*-**26**, 122592-65-8; *anti*-**26** (acetonide, 124781-56-2; *trans*-**27**, 124781-50-6; *cis*-**27**, 124781-51-7; **30**, 34485-82-0; *anti*-**31**, 124781-52-8; *syn*-**31**, 124781-53-9; **32** (Y = H), 556-52-5; **32** (Y = MOM), 45631-57-0; *anti*-**33** (Y = H), 124781-57-3; *syn*-**33** (Y = H), 124781-58-4; *anti*-**33** (Y = MOM), 124781-59-5; *syn*-**33** (Y = MOM), 124820-65-1; **34**, 7160-77-2; **35**, 81617-08-5; **36a**, 124781-61-9; **36b**, 124781-62-0; **37**, 124781-60-8; DBB, 1625-91-8; LDBB, 61217-61-6; PhSMe, 100-68-5; *p*-$MeOC_6H_4CHO$, 123-11-5; Me_2CHCHO, 78-84-2; *p*-$C_6H_{11}CHO$, 2043-61-0; CH_2=CHCHO, 107-02-8; *n*-$C_6H_{13}CHO$, 111-71-7; (*E*)-MeCH=CHCHO, 123-73-9; (*E*)-PhCH=CHCHO, 14371-10-9; Me_2CH=CHCHO, 107-86-8; $Ti(i\text{-}PrO)_4$, 546-68-9; $CeCl_3$, 7790-86-5; cyclohexanone, 108-94-1; 1-acetylcyclohexene, 932-66-1; 2-cyclohexen-1-one, 930-68-7.

Supplementary Material Available: ^1H NMR spectra for **15i**, **15k**, **15l**, *anti*-**15l**, **15m**, **15n**, **17**, **18**, **19**, **23**, **26**, *anti*-**26**, *syn*-**36**, *anti*-**36**, **33** (Y = MOM), **33** (Y = H), **34**, **36ab**, **36a**, and **37** (20 pages). Ordering information is given on any current masthead page.

Geometrical Dependence of γ-Trimethylsilyl Groups on Norbornyl Solvolyses. Rapid-Injection Kinetic Methods for Solvolyses of Unstable Mesylates

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Solvolytic rate constants in ethanol and aqueous ethanol mixtures are reported for solvolyses of unstable mesylates, prepared in situ from *tert*-butyl alcohol, and the following 6-trimethylsilyl (TMS) substituted 2-*exo*-norbornanols: 6-*exo*- and 6-*endo*-(trimethylsilyl)-substituted and 6,6-bis(trimethylsilyl)-substituted. These kinetic data for ethanol at 25 °C show similar relative rates to those observed for solvolyses of the corresponding *p*-nitrobenzoates in 97% w/w trifluoroethanol/water at 100 °C; there are up to ca. 100-fold larger rate enhancements due to γ-silicon than those previously reported for acyclic and monocyclic systems; e.g. in ethanol 3.3×10^4 for 6-*exo*-(trimethylsilyl)-2-*exo*-norbornyl mesylate; these results support recent experimental and theoretical studies showing that a *W* conformation is preferred. In contrast, for solvolyses of the corresponding 2-*endo*-brosylates in 80% ethanol/water and in 97% trifluoroethanol, the 6-*exo*-TMS substituent shows only a 2-4-fold rate enhancement, and the 6-*endo*-TMS substituent shows rate retardation. Additional rate constants are reported for conventional solvolyses of mesylates of 1-adamantanol, 2-*exo*-norbornanol, and 6-*exo*-(trimethylsilyl)-2-*endo*-norbornanol. These data for 6-*exo*-TMS compounds establish a 2-*exo*-/2-*endo*-norbornyl rate ratio of $>10^6$, the largest observed for an unhindered secondary system.

The kinetic effects of γ-silicon substituents on solvolyses of 2-*exo*-norbornyl mesylates (methanesulfonates) are much larger than those previously reported for solvolyses of secondary acyclic[1a] and monocyclic substrates,[1b,2] and the bicyclic, trimethylsilyl (TMS) substituted compounds (**1-3**, X = OBs) could not be isolated.[3] Also, despite the importance of solvolyses of *tert*-butyl substrates (**4**),[4] few kinetic data for these sulfonates have previously been obtained because they are too unstable to isolate;[5] a relatively slow elimination reaction of *tert*-butyl tosylate has previously been examined in acetonitrile at 0 °C ($k = 1.8 \times 10^{-4}$ s^{-1}).[5a] We now report a procedure, based on convenient syntheses from alcohols[5b,6] and on rapid-injection, conductimetric methods, for obtaining a wide range of these data. Results will be compared with those for conventional solvolyses of other mesylates (**5**, **6**), with solvolyses of corresponding *p*-nitrobenzoates (**1-3**, **6**, X = *p*-nitrobenzoate), and also with solvolyses of 6-TMS-substituted 2-*endo*-norbornyl brosylates (*p*-bromobenzenesulfonates) (**7-10**).

The norbornyl framework acts as a relatively rigid backbone, providing known relative orientations of the TMS substituents and the leaving groups. The results reveal large variations in the geometrical dependence of the substituent effects of γ-TMS groups, and supplement an on-going project on the relative stabilities of TMS-substituted norbornyl cations.[3]

Results

The mesylates of interest were sufficiently stable (i.e. for several hours) that ca. 1 M solutions could be prepared in dichloromethane at −10 °C.[6] Direct injections of a few microliters of these cold solutions into the rapidly stirred, thermostatted solvolysis medium apparently caused local supersaturation, leading to unreliable kinetic data particularly for the more lipophilic substrates, e.g. even for 1-adamantyl mesylate (**5**), which can be isolated as a crystalline solid[6] and studied by conventional kinetic methods.[7a] Reliable kinetic data for solvolyses of **1-4** in

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