H, ArH), 6.89 (d, 2 H, J = 9 Hz, ArH ortho to OH), 5.16 (s, 1 H, ArOH), 3.89 (s, 2 H, CH_2); MS 284 (100, M^+), 265 (11), 252 (19), 239 (16), 207 (16); HRMS ($C_{21}H_{16}O$) calcd/found 284.1201/284.1199.

1,3-Diethyl-2-(4-hydroxyphenyl)indene (32). Purification was achieved by flash chromatography (7:3 hexane–EtOAc), affording a clear, viscous oil (110 mg, 83%): ^{1}H NMR ($CDCl_3$) δ 7.50–7.25 (m, 4 H, ArH), 7.22 (d, 2 H, J = 9 Hz, ArH meta to OH), 6.89 (d, 2 H, J = 9 Hz, ArH ortho to OH), 4.86 (s, 1 H, ArOH), 3.86 (t, 1 H, J = 5 Hz, $CHCH_2CH_3$), 2.66 (q, 2 H, J = 8 Hz, $=CCH_2CH_3$), 2.05–1.57 (m, 2 H, $CHCH_2CH_3$), 0.47 (q, 3 H, J = 7 Hz, $CHCH_2CH_3$); MS 264 (18, M^+), 235 (30), 41 (100); HRMS ($C_{19}H_{20}O$) calcd/found 264.1514/264.1519.

Preparation of Hydroxyindenones 12, 20, and 21. Demethylation of methoxyindenones **11**, **17**, and **18** was performed in molten pyridine hydrochloride, as previously described,[26,2a] providing hydroxyindenones **12**, **20**, and **21**, respectively.

2-Phenyl-3-ethyl-6-hydroxyindenone (12). The crude product was purified by flash chromatography (4:1 hexane–EtOAc), followed by recrystallization from CCl_4–pentane. Lustrous, dark purple-red flakes (30 mg, 46%) were obtained: mp 118–120 °C; ^{1}H NMR (acetone-d_6) δ 8.01 (s, 1 H, ArOH), 7.45–7.30 (m, 5 H, ArH), 7.21 (d, 1 H, J = 8 Hz, ArH on C-4), 6.95 (d, 1 H, J = 2 Hz, ArH on C-7), 6.90 (dd, 1 H, J = 8, 2 Hz, ArH on C-5), 2.76 (q, 2 H, J = 8 Hz, CH_2CH_3), 1.32 (t, 3 H, J = 8 Hz, CH_2CH_3); MS 250 (100, M^+), 235 (20), 207 (16); HRMS ($C_{17}H_{14}O_2$) calcd/found 250.0994/250.0988.

(26) Sheehan, J. C.; Erman, W. F.; Cruickshank, P. A. *J. Am. Chem. Soc.* **1957**, *79*, 147.

2-(4-Hydroxyphenyl)-3-ethylindenone (20). The crude product was purified by flash chromatography (7:3 hexane–EtOAc), followed by recrystallization (hexane–EtOAc). Dark red prisms (44 mg, 21%) were obtained: mp 144–147 °C; ^{1}H NMR ($CDCl_3$) δ 7.48 (d, 1 H, J = 7 Hz, ArH on C-7), 7.40 (t, 1 H, J = 7 Hz, ArH on C-5), 7.28 (d, 2 H, J = 9 Hz, ArH meta to OH), 7.24 (t?, 1 H, J = 7 Hz, ArH on C-6), 7.17 (d, 1 H, J = 7 Hz, ArH on C-4), 6.90 (d, 2 H, J = 9 Hz, ArH ortho to OH), 4.90 (s, 1 H, ArOH), 2.72 (q, 2 H, J = 8 Hz, CH_2CH_3), 1.33 (t, 3 H, J = 8 Hz, CH_2CH_3); MS 250 (100, M^+), 235 (36), 217 (11), 207 (28), 189 (11); HRMS ($C_{17}H_{14}O_2$) calcd/found 250.0994/250.0995.

2-(4-Hydroxyphenyl)-3-phenylindenone (21). Purification was achieved by flash chromatography (7:3 hexane–EtOAc), followed by recrystallization from ether–hexane at −30 °C. A red powder was obtained (200 mg, 68%): mp 165–166 °C; IR (KBr) 3400, 1700, 1610, 1590, 1510 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.56 (d, 1 H, J = 7 Hz, ArH on C-7), 7.45–7.21 (m, 7 H, ArH), 7.17 (d, 2 H, J = 9 Hz, ArH meta to OH), 7.11 (d, 1 H, J = 7 Hz, ArH on C-4), 6.73 (d, 2 H, J = 9 Hz, ArH ortho to OH), 4.95 (s, 1 H, ArOH); MS 298 (100, M^+), 281 (60), 269 (40), 252 (32), 239 (64); HRMS ($C_{21}H_{14}O_2$) calcd/found 298.0989/298.0994.

Acknowledgment. We are grateful for support of this research through a grant from the National Institutes of Health (PHS 5R01 DK 15556). High-field NMR spectra and high-resolution mass spectra were obtained on instruments supported by grants from the National Institutes of Health (RR 02299 and GM 27029, respectively). We are thankful for the assistance of Martin G. Pomper and Nathaniel S. Finney.

Substituted Lithium (*E*)-3-Lithio-3-tosyl-2-propenolates: Useful Intermediates in Organic Synthesis†

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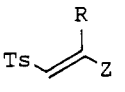
Received July 7, 1988

The lithiation of substituted tosylated epoxides **7** derived from allylic sulfones with methyllithium leads to lithium (*E*)-3-lithio-3-tosyl-2-propenolates **5** in a stereoselective manner. The further reaction of these intermediates with different electrophilic reagents (water, deuterium oxide, alkyl halides such as methyl iodide, allyl bromide, or methallyl chloride, and aldehydes such as crotonaldehyde, isobutyraldehyde, or benzaldehyde) in the presence or not of an additive [a copper(I) or magnesium salt and/or tetramethylethylenediamine] affords the functionalized tosylated allylic alcohols **10** in a regio- and stereoselective manner. The oxidation of primary alcohols **10** with manganese dioxide yields the corresponding α,β-unsaturated aldehydes **12**. When enediols **10** are treated with *p*-toluenesulfonic acid, the corresponding tosylated 2,5-dihydrofurans **13** are prepared. Tosylated furans **14** are isolated by oxidative cyclization of diols **10** using pyridinium chlorochromate (PCC) or manganese dioxide followed by dehydration with *p*-toluenesulfonic acid. Finally, for primary diols **10** (R^2 = H), the above-described PCC oxidation leads to the corresponding tosylated α,β-butenolides **16**.

Introduction

The chemistry of vinyl sulfones has been the subject of great attention in recent years due to their versatility in organic synthesis.[1-4] Recently,[5] we described a general method to prepare β-functionalized vinyl sulfones **2** by a tandem iodosulfonylation–dehydroiodination process starting from the appropriate electrophilic olefins **1**. Compounds of the type **2** are interesting in synthesis because they can act as β-acylvinyl cations[5,6] or anions[7,8] when in the last case they have been previously deprotonated. So, this dual behavior represents a typical case of normal or umpoled reactivity,[9] respectively. The lithiated derivatives of 4-tosylbutenone dimethyl ketal **3**[7] and of *N*-isopropyl-3-tosylacrylamide **4**[8] have been recently used as

1



2

R = H, Me
Z = CHO, COMe, CO_2H, CO_2Me, CONHPr, $CON(CH_2)_5$, CN

† Dedicated to Professor E. J. Corey on his 60th birthday.

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(1) For reviews, see: (a) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019. (b) Schank, K. In *Methoden der Organischen Chemie* (*Houben-Weyl*); Georg Thieme Verlag: Stuttgart, 1985; Vol. E/11, pp 1132–1298.

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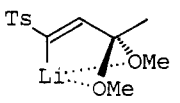
Table I. Preparation of Intermediates 5 and Their Reaction with Electrophiles E^+. Isolation of Products 10

		reactn condtns		product 10		
entry	epoxide 7	T, °C; additive	electrophile E^+	no.	yield,[a] %	mp,[b] °C, or R_f[c]
1	7a	−20; −	H_2O	10aa	89	120–122[d]
2	7a	−20; −	D_2O	10ab	93	120–122
3	7a	−40; TMEDA/CuI	MeI	10ac	87	0.29
4	7a	−20; TMEDA/CuI	CH_2=$CHCH_2Br$	10ad	32	0.40
5	7a	−20; TMEDA/CuCN	CH_2=$C(Me)CH_2Cl$	10ae	49	0.46
6	7a	−20; TMEDA	(*E*)-CH_3CH=$CHCHO$	10af	36 (90)[e]	0.27
7	7a	−20; $MgBr_2$	*i*-PrCHO	10ag	56 (88)[e]	120–122
8	7a	−20; TMEDA	*i*-PrCHO	10ag	98[e]	
9	7a	−20; $MgBr_2$	PhCHO	10ah	63	0.38
10	7a	−20; TMEDA	PhCHO	10ah	88[e]	
11	7b	−20; −	H_2O	10ba	88	0.38
12	7b	−20; −	D_2O	10bb	90	0.38
13	7b	−40; TMEDA	*i*-PrCHO	10bg	67[f]	102–104
14	7b	−20; $MgBr_2$	PhCHO	10bh	90[g]	0.40, 0.44
15	7b	−40; TMEDA	PhCHO	10bh	92[h]	
16	7c	−20; −	H_2O	10ca	88	106–107[i]
17	7c	−20; −	D_2O	10cb	84	106–107
18	7c	−35; TMEDA/CuI	CH_2=$CHCH_2Br$	10cd	41	0.45
19	7c	−40; $MgBr_2$	*i*-PrCHO	10cg	60	0.38
20	7c	−20; $MgBr_2$	PhCHO	10ch	75	0.42

[a] Isolated yield after flash chromatography (silica gel, hexane/ether) based on the starting expoxide 7. [b] From hexane/dichloromethane. [c] For oils; silica gel, hexane/ether, 1/10. [d] Literature[17] mp 120–122 °C. [e] Isolated crude yield; the product was homogeneous by TLC and pure by NMR. [f] Diastereoisomer mixture: 40/60 (from 300-MHz ^1H NMR; when the reaction was carried out at −78 °C, a 25/75 mixture (from ^1H NMR) was obtained. [g] Diastereoisomer mixture: 55/45 (from ^1H NMR). [h] Diastereoisomer mixture: 36/64 (from ^1H NMR); when the reaction was carried out at −78 °C, a 30/70 mixture (from ^1H NMR) was obtained. [i] Literature[17] mp 105–107 °C.

β-acylvinyl anion equivalents[10] in organic synthesis, and they have been shown to be interesting synthons for the preparation of different functionalized vinylic sulfones as well as cyclic systems such as furans, cyclopentenones, and α,β-butenolides.



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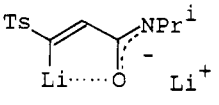

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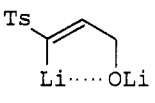
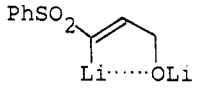


5a

Our interest in anions derived from β-functionalized vinyl sulfones of the type **3** or **4** prompted us to study the corresponding allyl alcohol derivatives **5**.[11] Ten years ago, Eisch and Galle[12] reported the preparation of **6**, one intermediate of the type **5**, which was chemically characterized by reaction with deuterium oxide and trimethylchlorosilane. These authors pointed out the multifunctional character of **6** and predicted its possibilities in synthesis. However, to our knowledge, they never reported a further study on this topic.



6

In the present paper, we describe (a) the generalization of the preparation of substituted tosylated dianions of the type **5**; (b) the possibilities in organic synthesis of such intermediates by reaction with electrophiles; and (c) the ability to transform the prepared functionalized allylic alcohols into other acyclic and cyclic products.

Results and Discussion

The treatment of the tosylated epoxides **7** (prepared by in situ *m*-chloroperbenzoic acid epoxidation of the corre-

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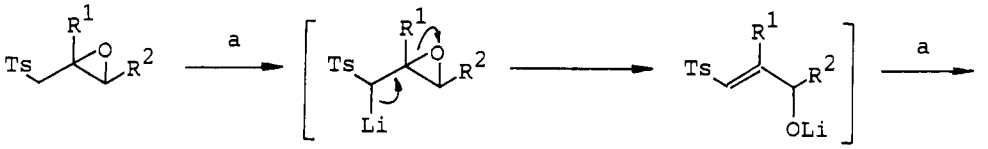
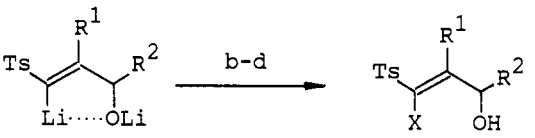
Scheme I[a]



7a, $R^1 = R^2 = H$
7b, $R^1 = H$, $R^2 = Me$
7c, $R^1 = Me$, $R^2 = H$

8 **9**



5a-c

10aa, $R^1 = R^2 = H$, X = H
10ab, $R^1 = R^2 = H$, X = D
10ac, $R^1 = R^2 = H$, X = Me
10ad, $R^1 = R^2 = H$, X = CH_2=$CHCH_2$
10ae, $R^1 = R^2 = H$, X = CH_2=C(Me)CH_2
10af, $R^1 = R^2 = H$, X = $CH_3CH\overset{E}{=}CHCHOH$
10ag, $R^1 = R^2 = H$, X = i-PrCHOH
10ah, $R^1 = R^2 = H$, X = PhCHOH
10ba, $R^1 = H$, $R^2 = Me$, X = H
10bb, $R^1 = H$, $R^2 = Me$, X = D
10bg, $R^1 = H$, $R^2 = Me$, X = i-PrCHOH
10bh, $R^1 = H$, $R^2 = Me$, X = PhCHOH
10ca, $R^1 = Me$, $R^2 = H$, X = H
10cb, $R^1 = Me$, $R^2 = H$, X = D
10cd, $R^1 = Me$, $R^2 = H$, X = CH_2=$CHCH_2$
10cg, $R^1 = Me$, $R^2 = H$, X = i-PrCHOH
10ch, $R^1 = Me$, $R^2 = H$, X = PhCHOH

[a] Reagents: (a) 2 MeLi/LiBr; (b) additive; (c) E^+ = H_2O, D_2O, MeI, CH_2=$CHCH_2Br$, CH_2=C(Me)CH_2Cl, (*E*)-CH_3CH=CHCHO, *i*-PrCHO, PhCHO; (d) HCl/H_2O.

sponding allylic sulfones[13]) with 2 equiv of methyllithium/lithium bromide in tetrahydrofuran at −20 °C yielded the corresponding dianion intermediates **5**, which were chemically characterized by hydrolysis or deuterolysis with deuterium oxide (Scheme I and Table I, entries 1, 2, 11, 12, 16, and 17). The reaction pathway involves the intermediates **8** and **9**, formed by (a) deprotonation at the α position with respect to the sulfone group in **7**, (b) β-elimination in **8** to yield **9**, and (c) final deprotontion to give the dianion **5**. The second lithiation on the allylic alcoholate **9** occurs regio- and stereoselectively, giving **5**, according to the expected[7] stabilization by intramolecular complexation.[10d,14] The in situ reaction of intermediates **5** with different electrophilic reagents, such as alkyl halides or aldehydes, has to occur in the presence of an additive [tetramethylethylenediamine (TMEDA) and/or a magnesium or copper(I) salt]. In the absence of this additive, the reaction does not taken place, with recovery after hydrolysis, of the corresponding alcohols **10aa**, **10ba**, and **10ca**.[15] From Table I it can be summarized that the alkylation reaction works only in the presence of TMEDA and a copper(I) salt, and the process with aldehydes needs the presence of TMEDA or magnesium bromide as additive.

The transformation **5** → **10** takes place through a S_E reaction with retention of configuration.[11,16] The stereochemistry of compounds **10** was confirmed not only by NMR experiments (negative nuclear Overhauser effect between R^1 = H or Me and the protons in the group X directly attached to the α position with respect to the sulfonyl group in products **10**) but also chemically: (a) in the reaction of intermediates **5** with water (Table I, entries 1, 11, and 16), the corresponding products **10aa**, **10ba**, and **10ca** were isolated with the same stereochemistry as the corresponding allylic alcohols arisen from the hydrolysis of intermediates **9** (Scheme I), when the reaction of **7** was carried out only with 1 equiv of methyllithium; (b) the cyclic products prepared from compounds **10** (see below) are consistent with the indicated stereochemistry for products **10** (Scheme I).

When the reaction of intermediate **5c** with isobutyraldehyde (compare with Table I, entry 19) was carried out in the presence of TMEDA, product **11** was isolated (48% yield) instead of the expected **10cg**. The obtention of **11** as a mixture of two diastereoisomers can take place by means of a dehydration of **10cg′**, precursor of **10cg**, in the

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Table II. Manganese Dioxide Oxidation of Alcohols 10 (R^2 = H) to Aldehydes 12

	starting alcohol 10			product 12		
entry	R^1	X	no.	no.	yield,[a] %	R_f[b]
1	H	H	**10aa**[c]	**12aa**	86	0.52[d]
2	H	Me	**10ac**	**12ac**	62[e]	0.51
3	H	CH_2=$CHCH_2$	**10ad**	**12ad**	95	0.66
4	H	CH_2=$C(Me)CH_2$	**10ae**	**12ae**	78	0.68
5	Me	H	**10ca**[c]	**12ca**	97	0.63
6	Me	CH_2=$CHCH_2$	**10cd**	**12cd**	74	0.70

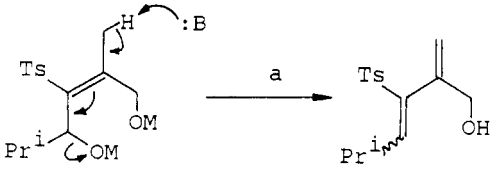
[a] Isolated yield after flash chromatography (silica gel, hexane/ether) based on the starting allyl alcohol **10**. [b] For oils; silica gel, hexane/ether, 1/10. [c] Prepared by acid hydrolysis of the corresponding intermediate of the type **9** (Scheme I) after addition of 1 equiv of methyllithium to the epoxide **7a** or **7b**. [d] Oil.[5] [e] Based on the epoxide **7a**, precursor of the alcohol **10** (overall yield).

Table III. Dihydrofurans 13 by Dehydration of Enediols 10

	starting diol 10				dihydrofurans 13		
entry	R^1	R^2	R^3	no.	no.	yield,[a] %	mp, °C, or R_f[b]
1	H	H	*i*-Pr	**10ag**	**13ag**	70	0.62
2	H	H	Ph	**10ah**	**13ah**	67	0.56
3	H	Me	Ph	**10bh**	**13bh**[c]	82[d]	0.66[e]
4	Me	H	Ph	**10ch**	**13ch**	63	110–112 (hexane/CH_2Cl_2)

[a] Isolated yield after flash chromatography (silica gel, hexane/ether) based on the starting epoxide **7** precursor of the diol **10** (overall yield). [b] For oils; silica gel, hexane/ether, 1/10. [c] BF_3·OEt_2 was used instead of *p*-toluenesulfonic acid (see text). [d] A ca. 55/45 mixture of two diastereoisomers was obtained (300-MHz ^{1}H NMR), the same ratio as in the case of the starting diol **10bh** (see footnote *g* in Table I). [e] Both diastereoisomers gave the same R_f value under these development conditions.

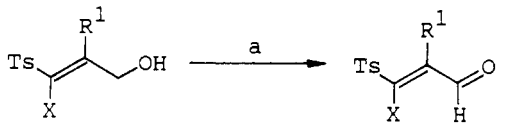
Scheme II[a]



10cg' (M = Li or MgBr) **11**

[a] Reagent: (a) HCl/H_2O.

Scheme III[a]



10 (R^2 = H)

12aa, R^1 = X = H
12ac, R^1 = H, X = Me
12ad, R^1 = H, X = CH_2=$CHCH_2$
12ae, R^1 = H, X = CH_2=$C(Me)CH_2$
12ca, R^1 = Me, X = H
12cd, R^1 = Me, X = CH_2=$CHCH_2$

[a] Reagent: (a) MnO_2.

basic reaction conditions (Scheme II).

The reaction of intermediates **5** with other electrophiles such as ethyl chloroformate, propylene and styrene oxide, cyclopentanone, or cyclohexenone/copper(I) iodide failed under different reaction conditions, yielding either the starting materials or an intractable reaction mixture.

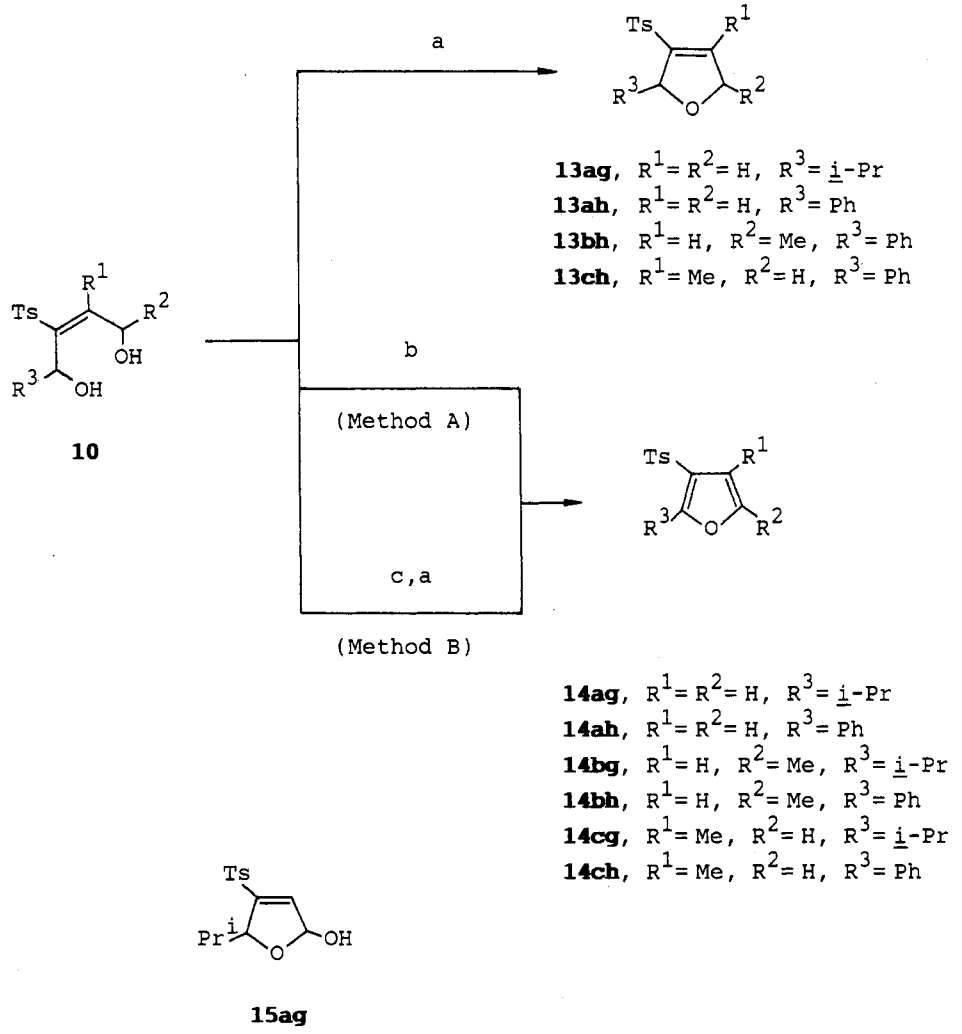
In order to explore the possibilities of compounds **10** in organic synthesis, we have initially investigated the oxidation of the substituted alcohols **10** with R^2 = H to the corresponding unknown aldehydes. So, the manganese dioxide oxidation[18] of the appropriate alcohols **10** in dichloromethane yielded the expected β-tosylated α,β-unsaturated aldehydes **12** (Scheme III and Table II). The interest in this class of compounds lies in their possible use as β-acylvinyl cation equivalents[5,6] or as electron-deficient olefins in Diels–Alder type reactions.[19] The stereochemistry in products **12** was assigned according to NMR data (coupling constants for **12aa** and negative nuclear Overhauser effect between R^1 = H or Me and the protons at the group X directly attached to the double bond) and, in the case of **12aa**, by comparison with the literature data.[5] It is noteworthy that compounds of the type **12** cannot be prepared by a tandem iodosulfonylation–dehydroiodination[5] without protection of the carbonyl group due to the oxidation of the aldehyde moiety under the reaction conditions. On the other hand, the corresponding ketones resulting from the oxidation of compounds **10** with R^2 = Me have been already prepared by alkylation of 4-lithio-4-tosylbutenone dimethyl ketal **3**.[7b]

The cyclization of diols **10**, derived from the reaction of intermediates **5** with aldehydes, was performed by treatment with *p*-toluenesulfonic acid in toluene at 90 °C (bath temperature); so, the corresponding dehydration took place giving the expected dihydrofurans **13** (Scheme IV and Table III). The transformation **10** → **13** can be alternatively carried out by using boron trifluoride etherate as cyclizing agent;[20] so, for instance, under these reaction conditions, the enediol **10bh** was transformed into the dihydrofuranic diastereoisomers **13bh** (Table III, entry 3). It has to be noted that in the obtention of products **13** we have never observed isomerization of the double bond,[20] so we think that the tosyl group prevents this process.

We have also studied the possibility of obtaining furans directly from the corresponding enediols **10** derived from aldehydes by an oxidative cyclization. So, when diols **10** with R^2 = Me were oxidized with pyridinium chlorochromate (PCC)[21] in dichloromethane (method A), the

(18) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; J. Wiley & Sons: New York, 1967; Vol. 1, p 637.
(19) (a) Sauer, J.; Wiest, H.; Mielert, A. *Chem. Ber.* **1964**, *97*, 3183. (b) Sauer, J.; Lang, D.; Wiest, H. *Chem. Ber.* **1964**, *97*, 3208. (c) Chiericato, M.; Dalla-Croce, P.; Carganico, G.; Maiorana, S. *J. Heterocycl. Chem.* **1979**, *16*, 383.
(20) Sato, F.; Kanbara, H.; Tanaka, Y. *Tetrahedron Lett.* **1984**, *25*, 5063.

Scheme IV[a]



15ag

[a] Reagents: (a) TsOH; (b) PCC; (c) MnO_2.

Table IV. Furans 14 by Oxidative Cyclization of Enediols 10

	starting diol 10					furan 14		
entry	R^1	R^2	R^3	no.	meth[a]	no.	yield,[b] %	mp, °C, or R_f[c]
1	H	H	*i*-Pr	**10ag**	B	**14ag**	51	0.74
2	H	H	Ph	**10ah**	B	**14ah**	45	0.65
3	H	Me	*i*-Pr	**10bg**	A	**14bg**	85	0.74
4	H	Me	Ph	**10bh**	A	**14bh**	90	141–143[d] (hexane/CH_2Cl_2)
5	Me	H	*i*-Pr	**10cg**	B[e]	**14cg**	65[f]	0.75
6	Me	H	Ph	**10ch**	B[g]	**14ch**	62[f]	100–102 (hexane/CH_2Cl_2)

[a] Method A: PCC. Method B: (a) MnO_2; (b) TsOH. [b] Isolated yield after flash chromatography (silica gel, hexane/ether) based on the epoxide **7** precursor of the diol **10** (overall yield). [c] For oils; silica gel, hexane/ether, 1/10. [d] Literature[7b] mp 142–143 °C. [e] The step b of this reaction (treatment with TsOH) was carried out at ambient temperature. [f] Based on the diol **10**. [g] The furan **14ch** was already isolated after the oxidation step with MnO_2.

expected furans **14** were isolated as the sole reaction product (Scheme IV and Table IV). For diols **10** with R^2 = H, the method does not give the expected furans **14** (see below); in this case, it is necessary to carry out the oxidation with manganese dioxide followed by dehydration using *p*-toluenesulfonic acid (method B) (Scheme IV and Table IV). Method B involves the corresponding dihydrofurans as intermediates, before the corresponding dehydration; so, in the case of the transformation **10ag** → **14ag**, the corresponding compound **15ag** was isolated by flash chromatography, after oxidation (60% yield), and characterized as the expected mixture of two diastereoisomers (Scheme IV and Experimental Section).

Finally, as it was mentioned above, the oxidation of diols **10** with R^2 = H by using PCC afforded directly the corresponding α,β-butenolides **16** (Scheme V and Table V). Compounds of this type[8] have found interesting applications in organic synthesis as synthetic equivalents of tosylpropiolate in Diels–Alder reactions.[22]

Conclusions

Substituted lithium 3-lithio-3-tosyl-2-propenolates of the type **5**, which can be considered as umpoled d^3 reagents,[9]

(21) (a) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647. (b) Burton, L. P.; White, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 3227. (c) Nishiyama, H.; Sasaki, M.; Itoh, K. *Chem. Lett.* **1981**, 1363.

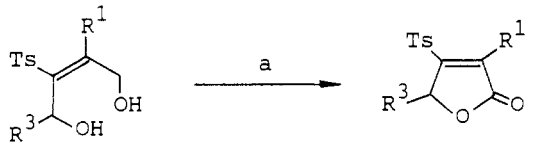
(22) Townsend, C. A.; Christensen, S. B.; Davis, S. G. *J. Chem. Soc., Perkin Trans. 1* **1988**, 839.

Table V. α,β-Butenolides 16 from Diols 10 (R^2 = H) by PCC Oxidation

	starting diol 10			butenolide 16		
entry	R^1	R^3	no.	no.	yield,[a] %	mp, °C
1	H	*i*-Pr	**10ag**	**16ag**	51	98–100[b] (hexane/$CHCl_3$)
2	H	Ph	**10ah**	**16ah**	56	145–147[c] (hexane/$CHCl_3$)
3	Me	*i*-Pr	**10cg**	**16cg**	75[d]	107–109 (hexane/CH_2Cl_2)
4	Me	Ph	**10ch**	**16ch**	78[d]	150–152 (hexane/ether)

[a] Isolated yield after flash chromatography (silica gel, hexane/ether) based on the starting epoxide 7 precursor of the diol 10 (overall yield). [b] Literature[8] mp 98–100 °C. [c] Literature[8] mp 145–147 °C. [d] Based on the starting diol 10.

Scheme V[a]



10 (R^2 = H)

16ag, R^1 = H, R^3 = *i*-Pr
16ah, R^1 = H, R^3 = Ph
16cg, R^1 = Me, R^3 = *i*-Pr
16ch, R^1 = Me, R^3 = Ph

[a] Reagent: (a) PCC.

are versatile synthons for the preparation of a wide series of 3-functionalized 3-tosylallyl alcohols **10** in a regio- and stereoselective manner. The obtained primary alcohols **10** (R^2 = H) are appropriate precursors for α,β-unsaturated aldehydes **12** by manganese dioxide oxidation. On the other hand, the *p*-toluenesulfonic acid cyclization of diols **10** derived from aldehydes yields dihydrofurans **13**, and the oxidative cyclization of the same starting materials affords tosylated furans **14** or butenolides **16**, depending on the structure of **10** and the oxidation agent (manganese dioxide or PCC). In all cases, the tosyl group fixes the regio- and stereochemistry of the initially lithiated double bond. We think that the prepared tosylated cyclic compounds are of interest because of their possibilities to be transformed into other organic molecules bearing or not the tosyl moiety.

Experimental Section

General Methods. For general information, see ref 7b. All NMR spectra were recorded in a Bruker AC-300 spectrometer, and in $CDCl_3$ as solvent.

Epoxy Sulfones 7. General Procedure.[13b] A suspension of sodium *p*-toluenesulfinate (13.5 g, 65 mmol) and the corresponding allylic halide (allyl and crotyl bromide, or methallyl chloride) (50 mmol) in methanol (75 mL) was refluxed for ca. 24 h. The solvent was then evaporated in vacuo (15 Torr), the residue dissolved in dichloromethane (100 mL), and the resulting solution washed with water and dried over anhydrous Na_2SO_4. To the resulting solution was added *m*-chloroperbenzoic acid (Aldrich, 85%; 10.3 g, 50 mmol), and the mixture was refluxed for ca. 24 h. The resulting precipitate was filtered off, and the solution was washed with an aqueous saturated solution of sodium carbonate, dried over anhydrous Na_2SO_4, and evaporated in vacuo (15 Torr) to give products **7**, which were recrystallized from hexane/ether. Isolated yields after recrystallization, melting points, and spectral data follow.

(Tosylmethyl)oxirane (7a): 70%; mp 51–53 °C; IR (Nujol) 3060, 1590 (CH=C), 1310, 1140 cm^{-1} (SO_2); ^1H NMR δ 2.40–2.60 (m with s at 2.46, 4 H, CH_3Ar, 1 H of CH_2O), 2.78 (m, 1 H, 1 H of CH_2O), 3.29 (m, 3 H, CH_2S, CHO), 7.38, 7.83 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 21.55 (CH_3), 45.74 (CH_2O, CHO), 59.38 (CH_2S), 128.06, 129.90, 136.16, 145.10 (aromatic C); MS, *m/z* (212 (M^+, 14), 155 (26), 139 (40), 92 (45), 91 (100), 89 (20), 65 (49), 63 (21), 57 (26), 39 (24), 31 (30).

1-Methyl-2-(tosylmethyl)oxirane (7b): 81%; 80/20 trans/cis-diastereoisomer mixture (300-Mz ^1H NMR); mp 43–45 °C [lit.[13b] mp 49–53 °C (trans isomer), 53–56 °C (cis isomer)]; IR (Nujol) 3060, 3040, 1590 (CH=C), 1310, 1140 cm^{-1} (SO_2); ^1H NMR (for the major trans isomer) δ 1.11 (d, J = 5 Hz, 3 H, CH_3CH), 2.33 (s, 3 H, CH_3Ar), 2.53 (qd, J = 5 Hz, 1 H, $CHCH_3$), 2.88 (ddd, J = 6.5, 5, 2 Hz, 1 H, $CHCH_2$), 3.13 (dd, J = 14.5, 5 Hz, 1 H, CHS), 3.23 (dd, J = 14.5, 6.5 Hz, 1 H, CHS), 7.26, 7.69 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR (for the trans isomer) δ 16.75 (CH_3CH), 21.40 (CH_3Ar), 52.19, 53.61 (2 CHO), 58.96 (CH_2), 127.93, 129.73, 136.22, 144.88 (aromatic C); MS, *m/z* 226 (M^+, 2), 91 (29), 71 (100), 65 (26), 45 (70), 43 (69).

1-Methyl-1-(tosylmethyl)oxirane (7c): 60%; mp 55–57 °C; IR (Nujol) 3040, 1590 (CH=C), 1315, 1140 cm^{-1} (SO_2); ^1H NMR δ 1.38 (s, 3 H, CH_3CO), 2.31 (s, 3 H, CH_3Ar), 2.45 (s, 2 H, CH_2O), 2.96, 3.41 (2 d, J = 14 Hz, 2 H, CH_2S), 7.24, 7.67 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 20.94, 21.19 (2 CH_3), 51.60 (CO), 52.44 (CH_2O), 63.19 (CH_2S), 127.61, 129.60, 136.59, 144.67 (aromatic C); MS, *m/z* 226 (M^+, 1), 139 (100), 92 (43), 91 (66), 65 (42), 43 (52), 41 (62), 39 (55).

Preparation of Intermediates 5 and Reaction with Electrophiles. Isolation of Products 10. General Procedure. To a solution of the epoxide **7** (1 mmol) and tetramethylethylenediamine (TMEDA, 2.2 mmol; see Table I) in THF (5 mL) was added an ethereal solution of methyllithium/lithium bromide (2.2 mmol) at temperatures ranging between −20 and −40 °C (see Table I) under argon. After 10 min of stirring, the corresponding magnesium or copper(I) salt (1.1 mmol; see Table I) was added and stirring was continued for 15 min at the same temperature. Then the corresponding electrophile (1.1 mmol) was added, and the reaction mixture was stirred overnight, allowing the temperature to rise to 20 °C. The resulting mixture was hydrolyzed with water and 1 N hydrochloric acid (in the case of using TMEDA alone or magnesium bromide) or a 0.2 N ammonia buffer solution [in the case of using a copper(I) salt] and extracted with dichloromethane and the organic layer washed with water, dried over anhydrous Na_2SO_4, and evaporated in vacuo (15 Torr). The resulting residue was purified by flash chromatography (silica gel, hexane/ether) and, when solid, recrystallized to afford products **10**. Yields and melting points or R_f values are reported in Table I. Spectral and analytical data follow.

(*E*)-3-Tosyl-2-propen-1-ol (10aa):[17] IR (Nujol) 3480 (OH), 3030, 1625, 1590 (CH=C), 1270, 1135 cm^{-1} (SO_2); ^1H NMR δ 2.10 (br s, 1 H, OH), 2.42 (s, 3 H, CH_3Ar), 4.34 (s, 2 H, CH_2), 6.62 (dt, J = 15, 1.5 Hz, 1 H, CHS), 6.99 (dt, J = 15, 3 Hz, 1 H, $CHCH_2$), 7.32, 7.74 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 21.46 (CH_3), 60.78 (CH_2), 127.56, 129.76, 137.06, 144.32 (aromatic C), 137.05, 144.47 (CH=CH); MS, *m/z* 212 (M^+, 16), 183 (84), 139 (48), 92 (60), 91 (100), 89 (32), 77 (22), 65 (68), 63 (33), 57 (21), 55 (21), 39 (34), 31 (40).

(*E*)-3-Deuterio-3-tosyl-2-propen-1-ol (10ab): IR (Nujol) 3050 (OH), 3050, 1615, 1595 (CH=C), 1280, 1140 cm^{-1} (SO_2); ^1H NMR δ 1.90 (br s, 1 H, OH), 2.44 (s, 3 H, CH_3Ar), 4.38 (s, 2 H, CH_2), 7.00 (s, 1 H, $CHCH_2$), 7.33, 7.76 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 21.27 (CH_3), 60.35 (CH_2), 127.32, 129.66, 137.01, 144.17 (aromatic C), 129.38 (t, J_{CD} = 27 Hz, CD), 145.24 ($CHCH_2$); MS, *m/z* 213 (M^+, 12), 184 (69), 139 (46), 107 (21), 92 (87), 91 (100), 77 (24), 65 (59), 63 (20) 58 (33).

(*E*)-3-Tosyl-2-buten-1-ol (10ac): IR (film) 3480 (OH), 3060, 3030, 1650, 1630, 1595 (CH=C), 1300, 1150, 1140 cm^{-1} (SO_2); ^1H NMR δ 1.71 (s, 3 H, CH_3C=CH), 2.31 (s, 3 H, CH_3Ar), 3.60 (br s, 1 H, OH), 4.19 (d, J = 6 Hz, 2 H, CH_2O), 6.82 (t, J = 6 Hz, 1 H, $CHCH_2$), 7.22, 7.62 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 11.45 (CH_3C=CH), 21.31 (CH_3Ar), 58.74 (CH_2), 127.91, 129.66, 135.08, 137.18, 139.15, 144.31 (aromatic C, CH=C); MS, *m/z* 226 (M^+, 8), 197 (100), 157 (47), 149 (24), 139 (87), 92 (74), 91 (80), 71 (71), 65 (35), 41 (28), 39 (22). Anal. Calcd for $C_{11}H_{14}O_3S$: C, 58.38; H, 6.23. Found: C, 58.1; H, 6.4.

(*E*)-3-Tosyl-2,5-hexadien-1-ol (10ad): IR ($CDCl_3$) 3500 (OH), 3090, 3070, 1635, 1595 (CH=C), 1300, 1150 cm^{-1} (SO_2); ^1H NMR δ 2.35 (s, 3 H, CH_3Ar), 2.50 (br s, 1 H, OH), 2.95 (d, J = 6 Hz, 2 H, CH_2CS), 4.25 (d, J = 5.5 Hz, 2 H, CH_2O), 4.8–5.0 (m, 2 H, CH_2C), 5.30–5.50 (m, 1 H, $CH=CH_2$), 6.98 (t, J = 6 Hz, 1 H, $CHCH_2O$), 7.24, 7.66 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 21.55 (CH_3), 30.61 (CH_2CS), 59.04 (CH_2O), 116.73 (CH_2=CH), 128.38, 129.80, 132.81, 135.83, 139.36, 141.22, 144.49 (aromatic C, CH=C, $CH=CH_2$); MS, m/z 252 (M^+, 0.5), 234 (12), 155 (43), 139 (53), 92 (41), 91 (72), 79 (23), 78 (32), 77 (55), 67 (37), 65 (76), 63 (21), 53 (20), 51 (22), 43 (21), 41 (100), 39 (77), 31 (26). Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.88; H, 6.39. Found: C, 61.6; H, 6.5.

(*E*)-5-Methyl-3-tosyl-2,5-hexadien-1-ol (10ae): IR ($CHCl_3$) 3500 (OH), 3080, 3060, 3020, 1640, 1590 (CH=C), 1300, 1145 cm^{-1} (SO_2); ^1H NMR δ 1.48 (s, 3 H, CH_3C=C), 2.34 (s, 4 H, CH_3Ar, OH), 2.92 (s, 2 H, CH_2CS), 4.20 (d, J = 6 Hz, 2 H, CH_2O), 4.43, 4.58 (2 s, 2 H, CH_2=C), 7.04 (t, J = 6 Hz, 1 H, $CHCH_2$), 7.22, 7.65 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 21.53, 22.12 (2 CH_3), 34.25 (CH_2CS), 59.35 (CH_2O), 112.23 (CH_2=C), 128.40, 129.68, 136.03, 139.29, 140.01, 141.91, 144.35 (aromatic C, CH=C, $C=CH_2$); MS, m/z 247 ($M^+ - H_2O$, 11), 139 (35), 109 (20), 95 (30), 93 (36), 92 (53), 91 (100), 81 (25), 79 (35), 77 (52), 67 (20), 65 (68), 63 (20), 55 (38), 53 (32), 51 (22), 43 (40), 41 (83), 39 (94), 31 (36). Anal. Calcd for $C_{14}H_{18}O_3S$: C, 63.13; H, 6.81. Found: C, 63.2; H, 6.6.

(*E,E*)-3-Tosyl-2,5-heptadiene-1,4-diol (10af): IR ($CDCl_3$) 3440 (OH), 3060, 3020, 1630, 1590 (CH=C), 1310, 1300, 1145 cm^{-1} (SO_2); ^1H NMR δ 1.43 (d, J = 5 Hz, 3 H, CH_3CH), 2.34 (s, 3 H, CH_3Ar), 3.95 (br s, 2 H, 2 OH), 4.35, 4.47 (2 dd, J = 16.5, 5 Hz, 2 H, CH_2O), 4.86 (d, J = 4 Hz, 1 H, CHO), 5.33 (m, 2 H, CH=CH), 6.99 (t, J = 5 Hz, 1 H, $CHCH_2$), 7.24, 7.63 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 17.27 (CH_3CH), 21.40 (CH_3Ar), 58.97 (CH_2), 68.48 (CHO), 128.13, 129.55, 129.61, 129.78, 136.12, 142.25, 142.97, 144.37 (aromatic C, CH=CH, CH=C); MS, m/z 264 ($M^+ - H_2O$, 14), 157 (21), 155 (25), 139 (38), 95 (42), 92 (37), 91 (100), 81 (29), 80 (33), 79 (63), 77 (49), 69 (31), 65 (69), 55 (49), 53 (44), 51 (23), 43 (41), 41 (75), 39 (71). Anal. Calcd for $C_{14}H_{18}O_4S$: C, 59.55; H, 6.42. Found: H, 59.2; H, 6.6.

(*E*)-5-Methyl-3-tosyl-2-hexene-1,4-diol (10ag): IR (Nujol) 3500, 3400 (OH), 3040, 1625, 1590 (CH=C), 1300, 1140 cm^{-1} (SO_2); ^1H NMR δ 0.64, 0.97 (2 d, J = 7 Hz, 6 H, 2 CH_3CH), 2.0 (septet, J = 7 Hz, 1 H, $CHCH_3$), 2.45 (s, 3 H, CH_3Ar), 3.05, 3.25 (2 br s, 2 H, 2 OH), 4.12 (d, J = 8.5 Hz, 1 H, CHO), 4.40, 4.52 (2 dd, J = 16, 5.5 Hz, 2 H, CH_2O), 7.03 (t, J = 5.5 Hz, 1 H, $CHCH_2$), 7.33, 7.76 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 18.80, 19.01 (2 CH_3CH), 21.60 (CH_3Ar), 33.41 ($CHCH_3$), 59.07 (CH_2O), 74.45 (CHO), 128.22, 129.90, 142.79, 144.20, 144.62 (aromatic C, CH=C); MS, m/z 241 ($M^+ - C_3H_7$, 16), 157 (50), 139 (52), 92 (35), 91 (95), 89 (23), 79 (22), 77 (25), 65 (58), 63 (21), 55 (30), 43 (100), 41 (86), 39 (58). Anal. Calcd for $C_{14}H_{20}O_4S$: C, 59.13; H, 7.09. Found: C, 59.1; H, 7.1.

(*E*)-1-Phenyl-2-tosyl-2-butene-1,4-diol (10ah): IR ($CDCl_3$) 3480 (OH) 3060, 3020, 1630, 1590 (CH=C), 1300, 1145 cm^{-1} (SO_2); ^1H NMR δ 2.20 (s, 3 H, CH_3Ar), 3.80, 4.65 (2 br s, 2 H, 2 OH), 3.97, 4.16 (2 dd, J = 16, 5 Hz, 2 H, CH_2O), 5.53 (s, 1 H, CHO), 6.90–7.10 (m, 8 H, Ph, $CHCH_2$, m-tolylic H), 7.46 (d, J = 8 Hz, 2 H, o-tolylic H); ^{13}C NMR δ 21.33 (CH_3), 58.62 (CH_2), 68.74 (CHO), 125.75, 127.26, 127.94, 128.03, 129.60, 135.77, 139.83, 143.58, 144.00, 144.31 (aromatic C, CH=C); MS, m/z 300 ($M^+ - H_2O$, 10), 145 (21), 131 (43), 128 (32), 116 (24), 115 (73), 105 (30), 92 (22), 91 (100), 89 (30), 79 (22), 77 (65), 65 (54), 63 (25), 51 (30), 39 (26). Anal. Calcd for $C_{17}H_{18}O_4S$: C, 64.13; H, 5.70. Found: C, 64.0; H, 5.7.

(*E*)-1-Tosyl-1-buten-3-ol (10ba): IR ($CHCl_3$) 3500 (OH), 3060, 3020, 1620, 1590 (CH=C), 1300, 1140 cm^{-1} (SO_2); ^1H NMR δ 1.26 (d, J = 6.5 Hz, 3 H, CH_3CH), 2.41 (s, 3 H, CH_3Ar), 3.45 (br s, 1 H, OH), 4.45 (m, 1 H, CHO), 6.56 (dd, J = 15, 2 Hz, 1 H, CHS), 6.91 (dd, J = 15, 3.5 Hz, 1 H, CHCHO), 7.31, 7.72 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 21.34, 22.02 (2 CH_3), 65.89 (CHO), 127.35, 129.73, 136.86, 144.30 (aromatic C), 128.82, 148.83 (CH=CH); MS, m/z 226 (M^+, 3), 183 (100), 139 (35), 92 (34), 91 (99), 71 (41), 65 (52), 63 (20), 45 (62), 43 (60), 41 (22), 39 (35). Anal. Calcd for $C_{11}H_{14}O_3S$: C, 58.38; H, 21.21. Found: C, 58.1; H, 21.3.

(*E*)-1-Deuterio-1-tosyl-1-buten-3-ol (10bb): IR ($CDCl_3$) 3520 (OH), 3080, 3040, 1620, 1600 (CH=C), 1310, 1150 cm^{-1} (SO_2); ^1H NMR δ 1.25 (d, J = 6.5 Hz, 3 H, CH_3CH), 2.40 (s, 3 H, CH_3Ar), 3.70 (br s, 1 H, OH), 4.45 (qd, J = 6.5, 3.5 Hz, 1 H, CHO), 6.85 (d, J = 3.5 Hz, 1 H, CHCHO), 7.30, 7.72 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 21.23, 21.89 (2 CH_3), 65.71 (CHO), 127.22, 129.63, 136.75, 144.19 (aromatic C), 128.35 (t, J_{CD} = 27 Hz, CD), 148.73 (CHCHO); MS, m/z 227 (M^+, 2), 184 (100), 139 (46), 92 (63), 91 (73), 72 (22), 65 (48), 45 (37), 43 (36), 39 (20).

(*E*)-6-Methyl-4-tosyl-3-heptene-2,5-diol (10bg): IR ($CDCl_3$) 3400 (OH), 3050, 3040, 1640, 1590 (CH=C), 1300, 1135 cm^{-1} (SO_2); ^1H NMR δ 0.52, 0.56, 0.89, 0.92 (4 d, J = 6.5 Hz, 6 H, 2 CH_3CHCHO), 1.23, 1.25 (2 d, J = 6 Hz, 3 H, CH_3CHO), 1.89, 2.05 [2 m, 1 H, $CH(CH_3)_2$], 2.36 (s, 3 H, CH_3Ar), 3.50 (br s, 2 H, 2 OH), 4.03, 4.06 [2 d, J = 8.5 Hz, 1 H, CH(OH)CS], 4.68, 4.81 [2 quintets, J = 6.5 Hz, 1 H, CH(OH)CH=C], 6.71, 6.79 (2 d, J = 8 Hz, 1 H, CH=CS), 7.22, 7.25, 7.66, 7.67 (4 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 18.97, 19.16, 19.19, 21.56, 22.30 (4 CH_3), 33.17, 33.81 (CHCHO), 63.49, 64.07 [CH(OH)CH_3], 74.29, 74.68 [CH(OH)CH], 128.11, 128.26, 129.82, 129.87, 136.37, 137.19, 142.87, 144.06, 144.51, 144.58, 145.85, 146.10 (aromatic C, CH=C); MS, m/z 255 ($M^+ - C_2H_3O$, 13), 157 (91), 155 (25), 139 (75), 99 (73), 92 (34), 91 (100), 65 (23), 43 (41).

(*E*)-1-Phenyl-2-tosyl-2-pentene-1,4-diol (10bh). Diastereoisomer of R_f 0.44: IR ($CDCl_3$) 3440 (OH), 3060, 3020, 1630, 1590 (CH=C), 1300, 1140 cm^{-1} (SO_2); ^1H NMR δ 1.17 (d, J = 6.5 Hz, 3 H, CH_3CH), 2.30 (s, 3 H, CH_3Ar), 3.35 (br s, 2 H, 2 OH), 4.55 (quintet, J = 6.5 Hz, 1 H, $CHCH_3$), 5.65 [s, 1 H, CH(OH)CS], 6.94 (d, J = 7 Hz, CHCHO), 7.00–7.20 (m, 7 H, aromatic H), 7.50 (d, J = 8 Hz, 2 H, aromatic H); ^{13}C NMR δ 21.51, 22.29 (2 CH_3), 64.45 [CH(OH)CH_3], 68.94 [CH(OH)CS], 125.84, 127.51, 128.03, 128.27, 129.73, 136.26, 140.41, 143.60, 144.37, 146.38 (aromatic C, CH=C); MS, m/z 314 ($M^+ - H_2O$, 22), 159 (42), 158 (38), 157 (29), 139 (27), 132 (76), 131 (53), 129 (22), 116 (21), 115 (49), 105 (46), 92 (25), 91 (100), 79 (24), 77 (57), 65 (40), 53 (23), 45 (26), 43 (46). Diastereoisomer of R_f 0.40: IR (film) 3480 (OH), 3060, 3030, 1635, 1590 (CH=C), 1300, 1140 cm^{-1} (SO_2); ^1H NMR δ 0.92 (d, J = 6.5 Hz, 3 H, CH_3CH), 2.25 (s, 3 H, CH_3Ar), 3.90 (br s, 2 H, 2 OH), 4.40 (quintet, J = 7 Hz, 1 H, $CHCH_3$), 5.59 [s, 1 H, CH(OH)CS], 6.86 (d, J = 7.5 Hz, 1 H, CHCHO), 7.00–7.20 (m, 7 H, aromatic H), 7.54 (d, J = 8 Hz, 2 H, aromatic H); ^{13}C NMR δ 21.41, 21.56 (2 CH_3), 63.49 $CHCH_3$), 68.41 [CH(OH)CS], 125.43, 127.24, 128.08, 128.87, 129.77, 135.65, 140.49, 144.49, 144.81, 146.22 (aromatic C, CH=C); MS, m/z 314 ($M^+ - H_2O$, 22), 159 (51), 158 (46), 157 (35), 139 (31), 132 (95), 131 (56), 129 (26), 116 (25), 115 (57), 105 (50), 92 (26), 91 (100), 79 (23), 77 (60), 65 (39), 53 (24), 45 (23), 43 (42).

(*E*)-2-Methyl-3-tosyl-2-propen-1-ol (10ca):[17] IR ($CDCl_3$) 3480 (OH), 3060, 1630, 1590 (CH=C), 1300, 1135 cm^{-1} (SO_2); ^1H NMR δ 2.02 (s, 3 H, CH_3CCH_2), 2.43 (s, 3 H, CH_3Ar), 2.97 (br s, 1 H, OH), 4.07 (s, 2 H, CH_2), 6.53 (s, 1 H, CHS), 7.32, 7.77 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 14.26 (CH_3CCH_2), 21.51 (CH_3Ar), 65.91 (CH_2), 123.91 (CHS), 127.04, 129.75, 138.93, 144.10 (aromatic C), 155.84 (CCH_2); MS, m/z 228 (M^+ + 2, 2), 226 (M^+, 35), 197 (20), 139 (66), 129 (24), 92 (67), 91 (100), 89 (21), 71 (69), 65 (67), 63 (25), 43 (29), 41 (57), 39 (64), 31 (35).

(*E*)-3-Deuterio-2-methyl-3-tosyl-2-propen-1-ol (10cb): IR ($CDCl_3$) 3480 (OH), 3050, 1620, 1590 (CH=C), 1300, 1145 cm^{-1} (SO_2); ^1H NMR δ 1.89 (s, 3 H, CH_3CCH_2), 2.30 (s, 3 H, CH_3Ar), 2.89 (br s, 1 H, OH), 3.95 (s, 2 H, CH_2), 7.19, 7.64 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 14.10 (CH_3CCH_2), 21.34 (CH_3Ar), 65.61 (CH_2), 123.35 (t, J_{CD} = 27.5 Hz, CD), 126.86, 129.66, 138.75, 144.02 (aromatic C), 156.02 (CCH_2); MS, m/z 229 (M^+ + 2, 5), 227 (M^+, 72), 209 (33), 198 (36), 143 (20), 139 (100), 130 (26), 92 (68), 91 (95), 72 (52), 65 (46), 42 (20).

(*E*)-2-Methyl-3-tosyl-2,5-hexadien-1-ol (10cd): IR (film) 3500 (OH), 3050, 1630, 1590 (CH=C), 1300, 1140 cm^{-1} (SO_2); ^1H NMR δ 2.20 (s, 3 H, CH_3CCH_2), 2.42 (s, 3 H, CH_3Ar), 2.50 (br s, 1 H, OH), 3.26 (d, J = 6 Hz, 2 H, CH_2CH), 4.16 (s, 2 H, CH_2O), 4.95–5.05 (m, 2 H, CH_2=C), 5.65–5.80 (m, 1 H, $CH=CH_2$), 7.30, 7.73 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 16.85 (CH_3C-CH_2), 21.38 (CH_3Ar), 32.58 (CH_2CH), 63.86 (CH_2O), 116.29 (CH_2=C), 127.24, 129.47, 135.11, 138.43, 143.89, 150.39 (aromatic C, C=C), 134.45 ($CH=CH_2$); MS, m/z 248 ($M^+ - H_2O$, 5), 157 (23), 139 (40), 93 (33), 92 (43), 91 (100), 79 (34), 77 (53), 65 (46), 55 (20), 53 (22), 41 (32), 39 (34). Anal. Calcd for $C_{14}H_{18}O_3S$: C, 63.13; H, 6.81. Found: C, 63.1; H, 6.9.

(*E*)-2,5-Dimethyl-3-tosyl-2-hexene-1,4-diol (10cg): IR ($CDCl_3$) 3500 (OH), 3060, 3030, 1630, 1600 (CH=C), 1300, 1150

cm^{-1} (SO_2); ^1H NMR δ 0.77, 1.02 (2 d, J = 6.5 Hz, 6 H, 2 CH_3CH), 1.86 (s, 3 H, CH_3CCH_2), 2.2–2.4 (m with s at 2.31, 4 H, $CHCH_3$, CH_3Ar), 4.06, 4.18 (2 d, J = 13 Hz, 2 H, CH_2), 4.35 (d, J = 10 Hz, 1 H, CHO), 7.20, 7.75 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 18.39, 19.64, 19.85, 21.49 (4 CH_3), 34.12 ($CHCH_3$), 63.30 (CH_2), 76.16 (CHO), 126.85, 129.54, 139.54, 140.11, 143.87, 152.00 (aromatic C, C=C); MS, m/z 255 ($M^+ - C_3H_7$, 36), 157 (100), 155 (20), 139 (66), 92 (20), 91 (61), 83 (20), 43 (27). Anal. Calcd for $C_{15}H_{22}O_4S$: C, 60.37; H, 7.43. Found: C, 60.5; H, 7.5.

(*E*)-3-Methyl-1-phenyl-2-tosyl-2-butene-1,4-diol (10ch): IR ($CHCl_3$) 3480 (OH), 3070, 3050, 1615, 1590 (CH=C), 1300, 1140 cm^{-1} (SO_2); ^1H NMR δ 2.04 (s, 3 H, CH_3CH_2), 2.25 (s, 3 H, CH_3Ar), 2.30 (br s, 2 H, 2 OH), 3.79, 3.99 (2 d, J = 13 Hz, 2 H, CH_2O), 5.98 (s, 1 H, CHO), 7.0–7.3 (m, 7 H, aromatic H), 7.49 (d, J = 8 Hz, 2 H, aromatic H); ^{13}C NMR δ 18.95 (CH_3CCH_2), 21.36 (CH_3Ar), 63.97 (CH_2), 70.12 (CHO), 125.34, 127.09, 128.20, 129.52, 138.34, 141.15, 141.54, 144.09, 153.93 (aromatic C, C=C); MS, m/z 314 ($M^+ - H_2O$, 5), 144 (100), 129 (23), 115 (20), 105 (47), 91 (77), 79 (25), 77 (76), 67 (69), 65 (43), 53 (20), 51 (33), 43 (32), 41 (26), 39 (42). Anal. Calcd for $C_{18}H_{20}O_4S$: C, 65.03; H, 6.06. Found: C, 65.0; H, 5.8.

(*Z*,*E*)-5-Methyl-2-methylidene-3-tosyl-3-hexen-1-ol (11): IR (film) 3500 (OH), 3060, 1640, 1610, 1590 (CH=C), 1300, 1140 cm^{-1} (SO_2); ^1H NMR (for the major isomer) δ 1.03 (d, J = 6.5 Hz, 6 H, 2 CH_3CH), 2.30–2.60 (m with a s at 2.42, 4 H, CH_3Ar, $CHCH_3$), 2.90 (br s, 1 H, OH), 4.14 (s, 2 H, CH_2O), 4.53, 5.39 (2 s, 2 H, CH_2=C), 6.80 (d, J = 10.5 Hz, 1 H, CH=CS), 7.29, 7.67 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 21.45, 21.92, 22.12 (3 CH_3), 27.34, 28.73 ($CHCH_3$), 64.91, 65.21 (CH_2O), 118.80, 119.57 (CH_2=C), 127.49, 128.37, 129.39, 129.47, 135.10, 139.78, 144.12, 149.50, 152.71 (aromatic C, C=CH, C=CH_2); MS, m/z 280 (M^+, 12), 185 (21), 183 (29), 167 (20), 149 (60), 139 (38), 125 (42), 109 (28), 107 (24), 105 (22), 93 (20), 92 (29), 91 (100), 83 (20), 81 (20), 79 (40), 77 (43), 69 (21), 65 (54), 57 (30), 55 (41), 53 (22), 43 (49), 41 (50), 39 (33).

Manganese Dioxide Oxidation of Alcohols 10 (R^2 = H). Isolation of α,β-Unsaturated Aldehydes 12. General Procedure. A suspension of the corresponding alcohol **10** (0.5 mmol) and manganese dioxide[18] (5 mmol) in dichloromethane (20 mL) was stirred for ca. 24 h. The resulting mixture was filtered and the filtrate evaporated in vacuo (15 Torr) to give the crude aldehydes **12**, which were purified by flash chromatography (silica gel, hexane/ether). Yields and R_f values for the oily products **12** are reported in Table II. Spectral and analytical data follow.

(*E*)-3-Tosyl-2-propanal (12aa). See ref 5.

(*E*)-3-Tosyl-2-butenal (12ac): IR ($CDCl_3$) 3050, 1610, 1590 (CH=C), 2760, 1675 (CH=O), 1320, 1130 cm^{-1} (SO_2); ^1H NMR δ 2.31 (d, J = 1 Hz, 3 H, CH_3CS), 2.47 (s, 3 H, CH_3Ar), 6.88 (dd, J = 6, 1 Hz, 1 H, $CHCHO$), 7.39, 7.77 (2 d, J = 8 Hz, 4 H, aromatic H), 10.01 (d, J = 6 Hz, 1 H, CHO); ^{13}C NMR δ 12.19 (CH_3CS), 21.60 (CH_3Ar), 128.75, 130.17, 133.73, 145.67 (aromatic C), 130.35, 155.99 (CH=C), 189.73 (C=O); MS, m/z 224 (M^+, 7), 139 (73), 92 (100), 91 (93), 89 (22), 69 (53), 65 (54), 63 (23), 41 (34), 39 (57). Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.90; H, 5.39. Found: C, 59.1; H, 5.4.

(*E*)-3-Tosyl-2,5-hexadienal (12ad): IR ($CDCl_3$) 3050, 1630, 1590 (CH=C), 2740, 1680 (CH=O), 1315, 1150 cm^{-1} (SO_2); ^1H NMR δ 2.38 (s, 3 H, CH_3Ar), 3.40 (d, J = 6 Hz, 2 H, CH_2CS), 4.90 (m, 2 H, CH_2=CH), 5.59 (m, 1 H, $CHCH_2$), 6.81 (d, J = 6.5 Hz, 1 H, $CHCHO$), 7.29, 7.68 (2 d, J = 8 Hz, 4 H, aromatic H), 9.92 (d, J = 6.5 Hz, 1 H, CHO); ^{13}C NMR δ 21.60 (CH_3), 30.48 (CH_2CS), 117.90 (CH_2=C), 128.92, 130.11, 131.53, 132.83, 134.20, 145.62, 157.05 (aromatic C, CH=C, CH=CH_2), 189.68 (C=O); MS, m/z 250 (M^+, 3), 221 (20), 157 (26), 139 (63), 95 (52), 92 (53), 91 (89), 89 (21), 67 (81), 66 (24), 65 (100), 41 (54), 39 (78). Anal. Calcd for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64. Found: C, 62.4; H, 5.8.

(*E*)-5-Methyl-3-tosyl-2,5-hexadienal (12ae): IR ($CDCl_3$) 3090, 3050, 1640, 1590 (CH=C), 2750, 1680 (CH=O), 1310, 1150 cm^{-1} (SO_2); ^1H NMR δ 1.59 (s, 3 H, CH_3CCH_2), 2.38 (s, 3 H, CH_3Ar), 3.35 (s, 2 H, CH_2CS), 4.49, 4.70 (2 s, 2 H, CH_2C), 6.88 (d, J = 7 Hz, 1 H, $CHCHO$), 7.28, 7.68 (2 d, J = 8 Hz, 4 H, aromatic H), 9.86 (d, J = 7 Hz, 1 H, CHO); ^{13}C NMR δ 21.66, 22.43 (2 CH_3), 34.08 (CH_2CS), 113.67 (CH_2=C), 128.98, 130.09, 132.70, 134.40, 140.55, 145.67, 157.16 (aromatic C, CH=C, C=CH_2), 190.04 (C=O); MS, m/z 249 ($M^+ - CH_3$, 2), 139 (23), 109 (29), 92 (20), 91 (47), 81 (44), 79 (66), 77 (26), 65 (58), 53 (37), 51 (21), 41 (74), 39 (100). Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.61; H, 6.10. Found: C, 63.5; H, 6.1.

(*E*)-2-Methyl-3-tosyl-2-propenal (12ca): IR ($CDCl_3$) 3030, 1615, 1590 (CH=C), 2730, 1690 (CH=O), 1310, 1140 cm^{-1} (SO_2); ^1H NMR δ 2.06 (s, 3 H, CH_3CCO), 2.34 (s, 3 H, CH_3Ar), 6.88 (q, J = 1.5 Hz, 1 H, CHCS), 7.27, 7.73 (2 d, J = 8 Hz, 4 H, aromatic H), 9.31 (s, 1 H, CHO); ^{13}C NMR δ 9.62 (CH_3CCO), 21.48 (CH_3Ar), 127.67, 130.08, 136.90, 145.15, 145.45, 146.53 (aromatic C, CH=C), 191.97 (C=O); MS, m/z 224 (M^+, 7), 139 (78), 92 (42), 91 (100), 65 (60), 63 (21), 41 (22), 39 (56). Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.90; H, 5.39. Found: C, 59.1; H, 5.4.

(*E*)-2-Methyl-3-tosyl-2,5-hexadienal (12cd): IR ($CDCl_3$) 3050, 1630, 1590 (CH=C), 2740, 1680 (CH=O), 1310, 1140 cm^{-1} (SO_2); ^1H NMR δ 2.07 (s, 3 H, CH_3CCO), 2.38 (s, 3 H, CH_3Ar), 3.62 (d, J = 6 Hz, 2 H, CH_2CS), 5.00, 5.11 (2 d, J = 15, 10 Hz, 2 H, CH_2=C), 5.80 (m, 1 H, CH=CH_2), 7.28, 7.71 (2 d, J = 8 Hz, 4 H, aromatic H), 9.94 (s, 1 H, CHO); ^{13}C NMR δ 12.33 (CH_3CCO), 21.66 (CH_3Ar), 31.10 (CH_2CS), 118.03 (CH_2=C), 128.19, 129.90, 136.90, 141.96, 145.20, 152.41 (aromatic C, C=C), 134.28 ($CHCH_2$), 191.61 (C=O); MS, m/z 264 (M^+, 2), 157 (21), 139 (45), 109 (56), 92 (44), 91 (100), 89 (22), 81 (75), 79 (95), 77 (50), 65 (74), 63 (25), 53 (50), 51 (30), 41 (42), 39 (50). Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.61, H, 6.10. Found: C, 63.6; H, 6.0.

Dehydration of Diols 10. Isolation of Dihydrofurans 13 Using *p*-Toluenesulfonic Acid. General Procedure. A solution of the corresponding diol **10** (5 mmol) and *p*-toluenesulfonic acid (ca. 50 mg, 0.25 mmol) in toluene (3 mL) was heated at ca. 90 °C for 24 h. The cooled mixture was then dissolved in dichloromethane (10 mL) and washed with a saturated aqueous solution of sodium hydrogen carbonate. The organic layer was decanted, dried over anhydrous Na_2SO_4, and evaporated in vacuo (15 Torr) to give the crude products **13**, which were purified by flash chromatography and recrystallized. Yields and melting points or R_f values for oily compounds are reported in Table III. Spectral and analytical data follow.

2-Isopropyl-3-tosyl-2,5-dihydrofuran (13ag): IR ($CHCl_3$) 3030, 1620, 1595 (CH=C), 1320, 1150 cm^{-1} (SO_2); ^1H NMR δ 0.62, 0.92 (2 d, J = 7 Hz, 6 H, 2 CH_3CH), 2.01 (m, 1 H, $CHCH_3$), 2.37 (s, 3 H, CH_3Ar), 4.62, 4.70 (2 m, 3 H, CH_2O, CHO), 6.74 (d, J = 2 Hz, 1 H, $CHCH_2$), 7.28, 7.70 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 14.11, 19.77 (2 CH_3CH), 21.54 (CH_3Ar), 31.70 ($CHCH_3$), 74.73 (CH_2O), 88.97 (CHO), 127.93, 129.88, 136.42, 139.23, 143.12, 144.90 (aromatic C, CH=C); MS, m/z 266 (M^+, 2), 223 (32), 131 (29), 92 (27), 91 (100), 65 (43), 43 (25), 41 (31), 39 (35). Anal. Calcd for $C_{14}H_{18}O_3S$: C, 63.13; H, 6.81. Found: C, 63.0; H, 6.7.

2-Phenyl-3-tosyl-2,5-dihydrofuran (13ah): IR ($CDCl_3$) 3060, 3030, 1620, 1595 (CH=C), 1315, 1150 cm^{-1} (SO_2); ^1H NMR δ 2.26 (s, 3 H, CH_3), 4.81 (ddd, J = 15.5, 4.5, 2 Hz, 1 H of CH_2O), 4.93 (ddd, J = 15.5, 6, 2 Hz, 1 H, 1 H of CH_2O), 5.80 (ddd, J = 6, 4.5, 2 Hz, 1 H, CHO), 6.90–7.25 (m, 10 H, aromatic H, $CHCH_2$); ^{13}C NMR δ 21.34 (CH_3), 74.59 (CH_2), 86.51 (CHO), 127.53, 127.67, 128.10, 128.37, 129.21, 136.01, 137.81, 139.26, 144.05, 144.56 (aromatic C, CH=C); MS, m/z 300 (M^+, 11), 145 (45), 144 (38), 117 (31), 116 (48), 115 (100), 105 (26), 91 (95), 89 (26), 77 (37), 65 (59), 63 (27), 51 (24), 39 (34). Anal. Calcd for $C_{17}H_{16}O_3S$: C, 67.97; H, 5.37. Found: C, 68.2; H, 5.3.

4-Methyl-2-phenyl-3-tosyl-2,5-dihydrofuran (13ch): IR ($CDCl_3$) 3060, 3020, 1640, 1595 (CH=C), 1315, 1150 cm^{-1} (SO_2); ^1H NMR δ 2.18, 2.25 (2 s, 6 H, 2 CH_3), 4.70 (dd, J = 15, 4 Hz, 1 H, 1 H of CH_2), 4.80 (dd, J = 15, 6 Hz, 1 H, 1 H of CH_2), 5.86 (m, 1 H, CHO), 6.90–7.30 (m, 9 H, aromatic H); ^{13}C NMR δ 11.30 (CH_3CCH_2), 21.41 (CH_3 Ar), 79.74 (CH_2), 89.07 (CHO), 127.18, 127.92, 128.12, 128.36, 129.19, 135.17, 137.79, 139.02, 143.81, 150.00 (aromatic C, C=C); MS, m/z 314 (M^+, 7), 159 (25), 158 (47), 129 (40), 128 (33), 115 (28), 105 (28), 91 (100), 77 (46), 65 (44), 51 (30), 43 (37), 39 (27). Anal. Calcd for $C_{18}H_{18}O_3S$: C, 68.76; H, 5.77. Found: C, 68.3; H, 5.9.

Dehydration of Diol 10bh with Boron Trifluoride Etherate. Isolation of Dihydrofuran 13bh. A solution of diol **10bh** (0.17 g, 0.5 mmol) in dichloromethane (5 mL) was added to a solution of boron trifluoride etherate (0.18 mL, 1.5 mmol) in dichloromethane (3 mL) under argon. After ca. 24 h of stirring, an aqueous saturated solution of sodium hydrogen carbonate (5 mL) was added to the resulting solution and the organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuo (15

Torr). The resulting residue was purified by flash chromatography (silica gel, hexane/ether) to afford *cis,trans*-5-methyl-2-phenyl-3-tosyl-2,5-dihydrofuran (**13bh**) as an oil: IR ($CDCl_3$) 3080, 3060, 1620, 1600 (CH=C), 1310, 1150 cm^{-1} (SO_2); ^1H NMR δ 1.27, 1.32 (2 d, J = 6.5 Hz, 3 H, CH_3CH), 2.16, 2.18 (2 s, 3 H, CH_3Ar), 4.98, 5.15 (2 m, 1 H, $CHCH_3$), 5.72, 5.81 (2 dd, J = 5, 2 Hz, 1 H, CHPh), 6.8–7.2 (m, 10 H, aromatic H, CHCHO); ^{13}C NMR δ 20.39, 20.93, 21.15 (CH_3CH, CH_3Ar), 80.73, 81.49 ($CHCH_3$), 85.70, 86.09 (CHPh), 127.26, 127.47, 127.79, 127.86, 127.94, 128.08, 128.17, 128.71, 129.04, 135.88, 135.92, 137.40, 142.94, 143.06, 143.80, 143.87, 143.98 (aromtic C, CH=C); MS, m/z 314 (M^+, 5), 159 (28), 116 (61), 115 (61), 105 (23), 91 (100), 89 (21), 77 (30), 65 (47), 51 (20), 43 (60), 39 (20).

Transformation of Diols 10 into Furans 14. Method A: PCC Oxidation. General Procedure. To a solution of the corresponding diol **10** (0.5 mmol) in wet dichloromethane (10 mL) was added pyridinium chlorochromate (0.65 g, 3 mmol), and the mixture was stirred for 2 h. The resulting suspension was filtered, the filtrate evaporated in vacuo (15 Torr), and the obtained residue purified by flash chromatography (silica gel, hexane/ether) to give the furans **14**.

Method B: Tandem MnO_2 Oxidation and Dehydration with *p*-Toluenesulfonic Acid. General Procedure. This method includes the procedure described for compounds **12** followed by dehydration of the crude intermediate of the type **15** using the methodology described for compounds **13**. Yields and melting points or R_f values are reported in Table IV. Spectral and analytical data follow.

2-Isopropyl-3-tosylfuran (14ag): IR ($CDCl_3$) 3150, 3120, 3060, 3020, 1590, 1560, 1510, 1485 (CH=C), 1320, 1140 cm^{-1} (SO_2); ^1H NMR δ 1.22 (d, J = 7 Hz, 6 H, 2 CH_3CH), 2.41 (s, 3 H, CH_3Ar), 3.75 (septet, J = 7 Hz, 1 H, $CHCH_3$), 6.56 (d, J = 2 Hz, 1 H, CHCHO), 7.26 (d, J = 2 Hz, 1 H, CHO), 7.31, 7.80 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 20.72 (2 CH_3CH), 21.51 (CH_3Ar), 26.50 ($CHCH_3$), 109.74 (CHCHO), 126.83, 129.78, 139.80, 143.92, 164.12 (aromatic C, C=C), 140.96 (CHO); MS, m/z 266 (M^+ + 2, 7), 264 (M^+, 100), 249 (53), 238 (37), 223 (20), 115 (24), 140 (49), 139 (52), 125 (59), 109 (35), 108 (60), 92 (31), 91 (97), 79 (31), 77 (25), 65 (27), 43 (20), 41 (22). Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.61; H, 6.10. Found: C, 63.6; H, 6.4.

2-Phenyl-3-tosylfuran (14ah): IR ($CDCl_3$) 3160, 3130, 3060, 3030, 1590, 1550, 1505 (CH=C), 1310, 1140 cm^{-1} (SO_2); ^1H NMR δ 2.33 (s, 3 H, CH_3), 6.83 (d, J = 1.5 Hz, 1 H, CHCHO), 7.1–7.9 (m, 10 H, aromatic H and CHO); ^{13}C NMR δ 21.45 (CH_3), 112.63 (CHCHO), 127.02, 128.16, 128.22, 128.61, 128.97, 129.52, 129.93, 138.94, 144.10 (aromatic C, C=C), 141.31 (CHO); MS, m/z 300 (M^+ + 2, 6), 298 (M^+, 87), 115 (100), 105 (20), 91 (32), 89 (20), 65 (23). Anal. Calcd for $C_{17}H_{14}O_3S$: C, 68.43; H, 4.73. Found: C, 68.2; H, 4.8.

2-Isopropyl-5-methyl-3-tosylfuran (14bg): IR ($CDCl_3$) 3120, 1590, 1550 (CH=C), 1320, 1150 cm^{-1} (SO_2); ^1H NMR δ 1.13 (d, J = 7 Hz, 6 H, 2 CH_3CH), 2.13 (s, 3 H, CH_3CO), 2.33 (s, 3 H, CH_3Ar), 3.64 (septet, J = 7 Hz, 1 H, $CHCH_3$), 6.04 (s, 1 H, CHCO), 7.22, 7.71 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 13.20, 20.88, 21.48 (4 CH_3), 26.35 ($CHCH_3$), 105.18 (CHCO), 121.02, 126.77, 129.72, 140.03, 143.72, 150.93, 162.38 (aromatic C); MS, m/z 280 (M^+ + 2, 4), 278 (M^+, 64), 263 (52), 140 (28), 139 (100), 123 (25), 122 (73), 108 (21), 107 (27), 91 (68), 77 (23), 65 (47), 43 (97), 39 (23). Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.72; H, 6.52. Found: C, 64.5; H, 6.6.

5-Methyl-2-phenyl-3-tosylfuran (14bh). See ref 7b.

2-Isopropyl-4-methyl-3-tosylfuran (14cg): IR ($CDCl_3$) 3080, 1590, 1530 (CH=C), 1330, 1160 cm^{-1} (SO_2); ^1H NMR δ 1.19 (d, J = 6.5 Hz, 6 H, 2 CH_3CH), 1.94 (s, 3 H, CH_3CCHO), 2.34 (s, 3 H, CH_3Ar), 3.83 (septet, J = 6.5 Hz, 1 H, $CHCH_3$), 6.97 (s, 1 H, CHO), 7.20, 7.70 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 8.86 (CH_3CCHO), 20.96 (CH_3CH), 21.51 (CH_3Ar), 29.67 ($CHCH_3$), 119.10, 126.75, 129.69, 129.85, 138.27, 139.90, 143.78 (aromatic C); MS, m/z 278 (M^+, 42), 263 (25), 155 (40), 139 (21), 138 (26), 139 (66), 123 (60), 111 (23), 92 (23), 91 (100), 79 (29), 77 (36), 65 (47), 63 (25), 55 (24), 43 (51), 41 (38), 39 (30). Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.72; H, 6.52. Found: C, 64.6; H, 6.5.

4-Methyl-2-phenyl-3-tosylfuran (14ch): IR (Nujol) 3060, 1635, 1590, 1540 (CH=C), 1310, 1150 cm^{-1} (SO_2); ^1H NMR δ 2.16 (s, 3 H, CH_3CCO), 2.36 (s, 3 H, CH_3Ar), 7.15–7.75 (m with 2 d at 7.19, 7.61, J = 8 Hz, 10 H, aromatic H and CHO); ^{13}C NMR δ 9.49 (CH_3CCHO), 21.50 (CH_3Ar), 126.80, 127.92, 128.33, 128.98, 129.48, 129.65, 129.79, 129.89, 139.53, 139.63, 143.86 (aromatic C); MS, m/z 314 (M^+ + 2, 6), 312 (M^+, 75), 185 (34), 149 (35), 129 (56), 128 (100), 127 (56), 105 (26), 103 (20), 102 (21), 101 (20), 91 (73), 89 (24), 77 (60), 71 (20), 70 (26), 65 (72), 63 (30), 57 (65), 55 (38), 51 (32), 43 (46), 41 (57), 39 (36). Anal. Calcd for $C_{18}H_{16}O_3S$: C, 69.21; H, 5.16. Found: C, 69.5; H, 5.0.

***trans,cis*-5-Hydroxy-2-isopropyl-3-tosyl-2,5-dihydrofuran (15ag)**: oil, R_f 0.52 (silica gel, hexane/ether, 1/10); IR ($CDCl_3$) 3480 (OH), 3060, 3040, 1620, 1600 (CH=C), 1315, 1150 cm^{-1} (SO_2); ^1H NMR δ 0.53, 0.63, 0.93, 0.95 (4 d, J = 7 Hz, 6 H, 2 CH_3CH), 2.04 (m, 1 H, $CHCH_3$), 2.37 (s, 3 H, CH_3Ar), 3.85 (br s, 1 H, OH), 4.71, 4.91 (q, J = 2 Hz and dt, J = 4.5, 2 Hz, CHOCS), 5.95 (m, 1 H, CHOH), 6.38 (m, 1 H, CHCS), 7.28, 7.71, 7.72 (3 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 13.99, 14.76, 19.88 (2 CH_3CH), 21.60 (CH_3Ar), 30.04, 30.62 ($CHCH_3$), 87.99, 88.53 (CHOC), 100.36, 101.31 (CHOH), 128.13, 128.94, 130.03, 135.77, 135.89, 136.33, 136.76, 137.76, 145.41, 147.95 (aromatic C, CH=C); MS, m/z 264 ($M^+ - H_2O$, 2), 222 (29), 139 (56), 115 (20), 107 (50), 92 (50), 91 (100), 83 (20), 77 (23), 65 (69), 57 (48), 55 (59), 43 (85), 41 (82), 39 (72).

Transformation of Diols 10 (R^2 = H) into α,β-Butenolides 16 by PCC Oxidation. General Procedure. The same method as it was described for furans **14** (method A) was used. Yields and melting points are reported in Table V. Spectral and analytical data follow.

4-Isopropyl-3-tosyl-α,β-butenolide (16ag). See ref 8.

4-Phenyl-3-tosyl-α,β-butenolide (16ah). See ref 8.

4-Isopropyl-2-methyl-3-tosyl-α,β-butenolide (16cg): IR ($CDCl_3$) 3030, 1590 (CH=C), 1750 (C=O), 1320, 1145 cm^{-1} (SO_2); ^1H NMR δ 0.42, 1.09 (2 d, J = 7 Hz, 6 H, 2 CH_3CH), 2.12 (d, J = 2 Hz, 3 H, CH_3CC=O), 2.30–2.50 (m with s at 2.41, 4 H, CH_3Ar, $CHCH_3$), 4.91 (septet, J = 2 Hz, 1 H, CHO), 7.35, 7.75 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR δ 10.22, 13.11 (2 CH_3CH), 20.18, 21.76 (2 CH_3C), 30.15 ($CHCH_3$), 85.30 (CHO), 128.00, 130.42, 136.20, 136.79, 146.33, 155.61 (aromatic C, C=C), 171.16 (C=O); MS, m/z 254 [(M^+ + 2) - C_3H_6, 6], 252 (100), 119 (24), 92 (29), 91 (58), 69 (45), 67 (26), 65 (36), 43 (46), 41 (46), 39 (39). Anal. Calcd for $C_{15}H_{18}O_4S$: C, 61.20; H, 6.16. Found: C, 61.0; H, 6.2.

2-Methyl-4-phenyl-3-tosyl-α,β-butenolide (16ch): IR (Nujol) 3060, 3030, 1650, 1590 (CH=C), 1770 (C=O), 1310, 1150 cm^{-1} (SO_2); ^1H NMR δ 2.36 (s, 6 H, 2 CH_3), 6.05 (q, J = 2 Hz, 1 H, CHO), 6.95–7.40 (m, 9 H, aromatic H); ^{13}C NMR δ 10.31 (CH_3CCO), 21.59 (CH_3Ar), 82.46 (CHO), 127.81, 127.89, 128.68, 129.73, 132.31, 135.71, 136.22, 145.58, 156.83 (aromatic C, C=C), 171.02 (C=O); MS, m/z 328 (M^+, 19), 185 (36), 173 (100), 149 (29), 145 (53), 128 (38), 117 (35), 105 (45), 91 (28), 77 (27), 67 (23). Anal. Calcd for $C_{18}H_{16}O_4S$: C, 65.83; H, 4.91. Found: C, 65.8; H, 5.0.

Acknowledgment. We thank Professor J. Barluenga, Departamento de Química Organometálica, Universidad de Oviedo, for financial support and Dr. P. Bernad, Servicio de Espectrometría de Masas, Universidad de Oviedo, for mass spectrometric work.

Registry No. **7a**, 118356-16-4; **7b** (cis isomer), 118356-17-5; **7b** (trans isomer), 118356-53-9; **7c**, 118356-18-6; **10aa**, 95314-83-3; **10ab**, 118356-19-7; **10ac**, 95924-40-6; **10ad**, 118356-20-0; **10ae**, 118356-21-1; **10af**, 118356-22-2; **10ag**, 118356-23-3; **10ah**, 118356-24-4; **10ba**, 118356-25-5; **10bb**, 118356-26-6; **10ag** (isomer 1), 118356-27-7; **10bg** (isomer 2), 118375-54-5; **10bh** (isomer 1), 118356-28-8; **10bh** (isomer 2), 118356-54-0; **10ca**, 95314-84-4; **10cb**, 118356-29-9; **10cd**, 118356-30-2; **10cg**, 118356-31-3; **10ch**, 118356-32-4; **11** (*E* isomer), 118356-33-5; **11** (*Z* isomer), 118356-34-6; **12aa**, 88726-04-9; **12ac**, 95924-37-1; **12ad**, 118356-35-7; **12ae**, 118356-36-8; **12ca**, 88726-05-0; **12cd**, 118356-37-9; **13ag**, 118356-38-0; **13ah**, 118356-39-1; **13bh** (isomer 1), 118356-40-4; **13bh** (isomer 2), 118356-55-1; **13ch**, 118356-41-5; **14ag**, 118356-42-6; **14ah**, 118356-43-7; **14bg**, 118356-44-8; **14bh**, 115563-21-8; **14cg**, 118356-45-9; **14ch**, 118356-46-0; **15ag** (isomer 1), 118356-47-1; **15ag** (isomer 2), 118356-48-2; **16ag**, 118356-49-3; **16ah**, 118356-50-6; **16cg**, 118356-51-7; **16ch**, 118356-52-8; CH_2=$CHCH_2Br$, 106-95-6; CH_2=$C(Me)CH_2Cl$, 563-47-3; (*E*)-CH_3CH:CHCHO, 123-73-9; *i*-PrCHO, 78-84-2; PhCHO, 100-52-7; sodium *p*-toluenesulfinate, 824-79-3; crotyl bromide, 4784-77-4.