o-Benzenedisulfonimide as Reusable Brønsted Acid Catalyst for Acid-Catalyzed Organic Reactions

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Received 10 January 2008; revised 17 January 2008

Abstract: Acid-catalyzed organic reactions, such as etherification, esterification, acetal synthesis, cleavage, and interconversion, and pinacol rearrangement were carried out in the presence of catalytic amounts of *o*-benzenedisulfonimide as Brønsted acid catalyst; the conditions were mild and selective. The catalyst was easily recovered and purified, ready to be used in further reactions, with economic and ecological advantages.

Key words: acid catalysis, ether synthesis, ester synthesis, acetal synthesis, pinacol rearrangement

Recently, we reported some preliminary encouraging results concerning the use of *o*-benzenedisulfonimide (**1**; Figure 1) in catalytic amounts as Brønsted acid in some acid-catalyzed organic reactions.[1a] Etherification, esterification and acetalization of selected examples were examined in view of the synthetic significance and simplicity of the dehydrative acid-catalyzed methods for their synthesis.

In this paper we wish to report on a more comprehensive study on the advantages of sulfonimide **1** as a nontoxic, nonvolatile, and noncorrosive recyclable acid catalyst in such synthetic procedures. A further valuable aspect is the easy recovery of **1** in high yield from the reaction mixture, due to its complete solubility in water, and its reuse without loss of catalytic activity in further and various reactions, with economic and ecological advantages. All the reactions considered here were conducted in open-air flasks, analytical grade solvents were used, and the only side product was water.

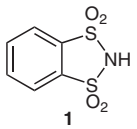

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Figure 1

o-Benzenedisulfonimide was described for the first time in 1921 and 1926 by Holleman[2] and Hurtley and Smiles,[3] respectively; more recently, Hendrickson,[4] Blaschette,[5] and Davis[6] and their co-workers reported modified procedures of synthesis. The key intermediate for its preparation is, however, *o*-benzenedisulfonyl chloride, which can be prepared starting from the commercially available dipotassium *o*-benzenedisulfonate,[3,6] anthranilic acid,[7] *o*-aminobenzenesulfonic acid,[2–5,8] and *o*-bis(methylsulfanyl)benzene.[9] Currently, both *o*-benzenedisulfonyl chloride and, very recently, *o*-benzenedisulfonimide are commercially available. The high acidity of Brønsted acid **1** is known (pK_a –4.1 at 20 °C),[10] but, to the best of our knowledge, it was shown for the first time to promote dehydrative reactions on various substrates.[1a]

There are many examples of acid-catalyzed reactions for the straightforward dehydrative syntheses of ethers, esters, and acetals from alcohols and suitable reactants, and they are regularly revised in many handbooks dealing with protective group chemistry. The functional groups introduced and the simplicity of the methods, both of synthesis and of cleavage, are extremely significant in organic chemistry.

The ether function is one of the most commonly used protective groups for the hydroxyl functionality, and many methods are available for its formation and removal under a wide variety of conditions.[11] Apart from the Williamson protocol, acid-catalyzed dehydration of alcohols represents the more direct synthesis of ethers, and has practical and economic advantages; protic acids, Lewis acids, metal catalysts,[12a–d] solid resins,[12e–h] supercritical fluids,[12i] ionic liquids,[12j,k] and surfactant-type catalysts[12l] have been reported as catalysts or solvents for dehydrative etherification and the interest for this reaction is still high today.

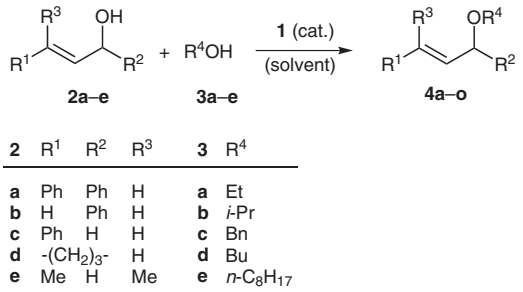
The success of literature methods of ether synthesis catalyzed by Brønsted acids via alcohol dehydration is very often dependent on the choice of the reactants (to avoid isomerization and elimination reactions) and of the protic acid catalyst; normally high acid concentrations and reaction temperatures are required.[11b,c] Metal catalysts, the use of which allows milder reaction conditions, are usually expensive;[12a–d] solid acid resins, although selective and recyclable, normally require high temperatures.[12e–g] Compared to these methods, our procedures are characterized by mild reaction conditions, short reaction times, and good selectivity.

The starting point of our research in this field was the recovery of ether derivatives in Heck-type arylation reactions of allylic alcohols in ethanol; such side products were obtained from the in situ arylated allylic alcohols, by dehydrative condensation with the solvent catalyzed by *o*-benzenedisulfonimide.[1b] First, we studied the etherification of the allylic alcohols 1,3-diphenylprop-2-en-1-ol

SYNTHESIS 2008, No. 9, pp 1379–1388
Advanced online publication: 27.03.2008
DOI: 10.1055/s-2008-1072564; Art ID: Z01308SS

(**2a**), 1-phenylprop-2-en-1-ol (**2b**), and 3-phenylprop-2-en-1-ol (**2c**) with the primary and secondary aliphatic alcohols **3a–e** (Scheme 1). Next, we applied the reaction to non-phenyl-substituted allylic alcohols, namely cyclohex-2-en-1-ol (**2d**) and 3-methylbut-2-en-1-ol (**2e**). All of our results are reported in Table 1.

During the course of the reactions we observed the exclusive formation of the mixed ethers **4a–o** only; these were isolated by flash chromatography of the crude residue and fully characterized. The reaction conditions seem to be very selective for the allylic systems studied.



2	R^1	R^2	R^3	3	R^4
a	Ph	Ph	H	**a**	Et
b	H	Ph	H	**b**	*i*-Pr
c	Ph	H	H	**c**	Bn
d	-$(CH_2)_3$-		H	**d**	Bu
e	Me	H	Me	**e**	*n*-C_8H_{17}

Scheme 1 *o*-Benzenedisulfonimide-catalyzed etherification

The reactions were carried out according to three different procedures: (a) in solution of the aliphatic alcohols **3a–d** (Method A; Table 1, entries 1, 2, 5, 6, 8, 9, 11); (b) in tetrahydrofuran as solvent (Method B; Table 1, entries 3, 4, 7, 14); (c) under solvent-free conditions (Method C; Table 1, entries 10, 12, 13, 15, 16). In methods B and C, the aliphatic alcohols **3** were used in stoichiometric

Table 1 *o*-Benzenedisulfonimide-Catalyzed Etherification of Allylic Alcohols **2a–e** with Aliphatic Alcohols **3a–e**

Entry	Reactants		Ratio	Amount	Method[a]	Temp	Time	Product **4**					Yield[b]
	2	**3**	**2/3**	**1** (mol%)		(°C)	(h)	**4**	R^1	R^2	R^3	R^4	(%)
1	**2a**	**3a**		5	A	r.t.	2	**4a**	Ph	Ph	H	Et	77 (81)
2	**2a**	**3b**		5	A	r.t.	0.25	**4b**	Ph	Ph	H	*i*-Pr	74 (77)
3	**2a**	**3c**	1:1	5	B	r.t.	1	**4c**	Ph	Ph	H	Bn	85 (90)
4	**2a**	**3d**	1:2	5	B	reflux	2.5	**4d**	Ph	Ph	H	Bu	70
5	**2b**	**3a**		5	A	60	15	**4e**	H	Ph	H	Et	56
								4f	Ph	H	H	Et	(**4e/4f** 1:1)[c]
6	**2b**	**3b**		5	A	60	15	**4g**	H	Ph	H	*i*-Pr	40
								4h	Ph	H	H	*i*-Pr	(**4g/4h** 1:2)[c]
7	**2b**	**3d**	1:2	5	B	reflux	55	**4i**	H	Ph	H	Bu	50
								4j	Ph	H	H	Bu	(**4i/4j** 1:2)[c]
8	**2b**	**3b**		20	A	reflux	8	**4h**	Ph	H	H	*i*-Pr	88
9	**2b**	**3b**		20[d]	A	reflux	8	**4h**	Ph	H	H	*i*-Pr	79
10	**2b**	**3c**	1:1.2	5	C	60	3	**4k**	Ph	H	H	Bn	60 (60)
11	**2c**	**3b**		20	A	60	7[e]	**4h**	Ph	H	H	*i*-Pr	41
12	**2c**	**3c**	1:1	10	C	60	4[e]	**4k**	Ph	H	H	Bn	50
13	**2d**	**3c**	1:1.2	5	C	60	1.5	**4l**	$(CH_2)_3$		H	Bn	75[f]
14	**2d**	**3d**	1:1.2	5	B	reflux	9	**4m**	$(CH_2)_3$		H	Bu	31[f]
15	**2e**	**3e**	1:1.2	5	C	60	6	**4n**	Me	H	Me	*n*-C_8H_{17}	28[c]
								4o	H	[g]	H	*n*-C_8H_{17}	(**4n/4o** 1:1)
16	**2e**	**3e**	2:1	5	C	60	3.5	**4n**	Me	H	Me	*n*-C_8H_{17}	40[c]
								4o	H	[g]	H	*n*-C_8H_{17}	(**4n/4o** 1:1.3)

[a] The reaction was carried out in the presence of an excess of alcohol **3** as solvent (Method A), in THF as solvent (Method B), and in the absence of solvent (Method C).
[b] Yields refer to pure isolated products; yields in parentheses are of isolated products from reactions carried out in the presence of 10 mol% **1**.
[c] Product ratio determined by GC analysis. The two isomers were isolated as pure products and partial mixture; spectroscopic data were obtained from pure products.
[d] Instead of **1**, 96% H_2SO_4 (20 mol%) was used as catalyst.
[e] By this time, reactant **2c** was no longer present.
[f] Bis(cyclohex-2-enyl) ether (**4p**) was detected in trace amounts (entry 13) or isolated (18%; entry 14).
[g] Ether **4o** bears two methyl groups in this position.

amounts or in slight excess relative to allylic alcohols **2**. All the methods were found to be suitable, and the choice depends on the nature of the reacting alcohols.

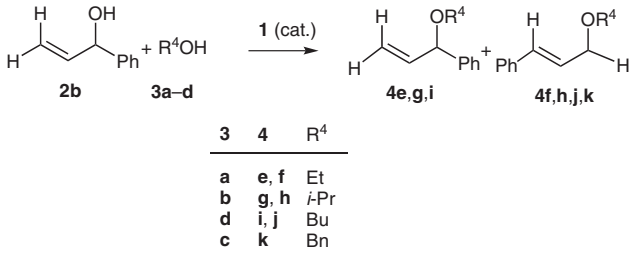
The preferred catalytic amount of *o*-benzenedisulfonimide (**1**) was 5 mol% (Table 1); in some cases, it was increased to 10 mol% to optimize the product yield (yield values in parentheses in Table 1, entries 1–3, 10). In all cases, *o*-benzenedisulfonimide (**1**) was recovered as a recyclable catalyst in high yield after workup of the reaction mixture. The reaction temperature was raised from room temperature (Table 1, entries 1–3) to 60 °C (entries 5, 6, 10–13, 15, 16) or reflux (entries 4, 7–9, 14), when the times required for conversion were too long at lower temperatures.

The etherification of 1,3-diphenylprop-2-en-1-ol (**2a**) proceeded under very mild conditions (r.t., or reflux in THF; Table 1, entries 1–4); the yields of the pure isolated ethers **4a–d** were good, and no traces of the symmetrical ethers were detected. High reactivity and selectivity can be explained by means of the resonance stabilization of the allylic and benzylic intermediate carbocation. We never detected or isolated traces of dialkyl ethers from the reaction mixtures; in fact, the reaction failed when it was applied to octan-1-ol to obtain the dioctyl ether by either Method B or C, at 90 °C, for prolonged reaction times, in the presence of 10 mol% **1** as catalyst. Furthermore, we carried out the reaction of 1,3-diphenylprop-2-en-1-ol (**2a**) with **3c** (**2a/3c**, 1:1; Method B) in the presence of an equimolar amount of 1,3-diphenylpropan-1-ol; after the workup, we isolated pure ether **4c** in 90% yield and the unchanged 1,3-diphenylpropan-1-ol in quantitative yield (see experimental section).

Lower reactivity was observed with allylic alcohols **2b** and **2c** (Table 1, entries 5–12): heating and prolonged reaction times were required (entries 5–10) and **2c** did not always undergo complete conversion into the desired products (entries 11 and 12). In the dehydrative etherification of 1-phenylprop-2-en-1-ol (**2b**), two isomers formed: beside the expected ethers **4e**, **4g**, and **4i**, compounds **4f**, **4h**, and **4j** were recovered, respectively (Table 1, entries 5–7; Methods A and B; Scheme 2). They derived by the well-known allylic rearrangement of the intermediate carbocation;[13] the reaction is an equilibrium, but in the reaction of **2b** with **3b**, we were able to optimize the reaction conditions, by addition of 20 mol% acid catalyst **1**, so that only the more stable primary ether **4h** was obtained in good yield (Table 1, entry 8).

Moreover, *E*-isomers were the only pure isolated products. To verify a possible role of the *o*-benzenedisulfonimide on such stereoselectivity, we repeated the reaction, using sulfuric acid as catalyst; the same reaction conditions gave the same result, but in lower yield (Table 1, entry 9, cf. entry 8).

From the reaction of **2b** with **3c**, only rearranged ether **4k** was obtained (Table 1, entry 10; Method C).



3	4	R^4
a	**e**, **f**	Et
b	**g**, **h**	*i*-Pr
d	**i**, **j**	Bu
c	**k**	Bn

Scheme 2

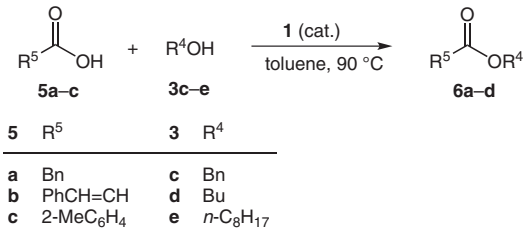
In the etherification of 3-phenylprop-2-en-1-ol (**2c**) with **3b** and **3c**, (*E*)-1-phenyl-3-isopropoxyprop-1-ene (**4h**) and (*E*)-1-phenyl-3-benzyloxyprop-1-ene (**4k**) were isolated, respectively, as pure products in modest yields (Table 1, entries 11 and 12).

The decreasing reactivity from **2a** to **2c** can be explained in terms of lower stabilization by resonance of the carbocation intermediate.

Finally, we applied these reaction conditions to non-phenyl-substituted allylic alcohols **2d** and **2e** (Table 1, entries 13–16); the results were not as good, but could be optimized. Cyclohex-2-en-1-ol (**2d**) was reacted with benzyl alcohol (**3c**) and butan-1-ol (**3d**) in the presence of 5 mol% of catalyst **1**, by Method C or B, respectively; this afforded pure ethers **4l** (75% yield; Table 1, entry 13) and **4m** (31% yield; entry 14). The symmetric bis(cyclohex-2-en-1-yl) ether formed as byproduct **4p** in the reaction mixture; it was also isolated in 18% yield (Table 1, entry 14). As expected, the etherification of 3-methylbut-2-en-1-ol (**2e**) with octan-1-ol (**3e**) furnished, along with prenyl octyl ether (**4n**), the rearranged ether 3-methyl-3-(octyloxy)but-1-ene (**4o**) by allylic rearrangement of the intermediate carbocation; the low yield could be improved only slightly by addition of an excess of the allylic alcohol (Method C; Table 1, entries 15 and 16).

Next, ester synthesis was examined. The dehydrative direct esterification of carboxylic acids **5a–c** with alcohols **3c–e** catalyzed by *o*-benzenedisulfonimide (**1**) (Scheme 3) was carried out in view of the synthetic relevance of the reaction both on laboratory and industrial scale.[14a,b,g] Silica-gel supported sodium hydrogen sulfate,[14c] acidic ionic liquids,[12j] surfactant-type Brønsted acids,[12l,14d] acidic solid resins,[14e,f] or Lewis acids[14h] have been used in recent applications of the reaction. Since it is an equilibrium process, the reaction is usually performed in the presence of a large excess of one of the reactants or with continuous removal of the water formed as byproduct; in our procedure both disadvantages were avoided.

We examined only a few examples (Scheme 3): the reagents were used in almost stoichiometric amounts, at 90 °C in toluene. Of the recyclable catalyst **1**, 20–30 mol% was used, in the absence of dehydrating agents; pure products were isolated by flash chromatography of the crude residue after basic washing of the reaction mixture to recover unchanged acids.



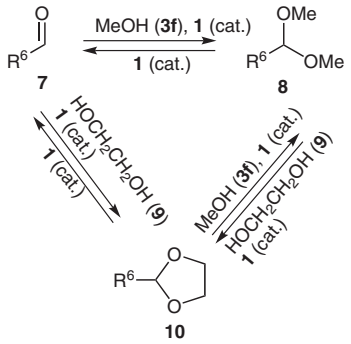
Scheme 3 *o*-Benzenedisulfonimide-catalyzed esterification

The results are listed in Table 2: they clearly show decreasing reactivity and product yields from the nonconjugated phenylacetic acid (**5a**; Table 2, entries 1 and 2) to the conjugated cinnamic acid (**5b**; entries 3 and 4; prolonged reaction times) and further on to the aromatic 2-methylbenzoic acid (**5c**; entry 6; no reaction was observed). Moreover, selective esterification of phenylacetic acid (**5a**) over cinnamic acid (**5b**) with butan-1-ol (**3d**) was achieved (Table 2, entry 5): acids **5a** and **5b** were used in equimolar amounts to react with **3d** (in slight excess) until GC analysis of the reaction mixture showed no further change; esters **6a** and **6d** were isolated in 89% and 9% yield, respectively, along with the unchanged starting acids **5a** (9%) and **5b** (88%), respectively. From all the reactions, *o*-benzenedisulfonimide (**1**) was recovered in high yield and reused as catalyst for other reactions.

To further explore the synthetic usefulness of *o*-benzenedisulfonimide (**1**), we carried out some acetalization, transacetalization, and acetal-cleavage reactions (Scheme 4, Table 3).

Acetalization of the carbonyl function of aldehydes or ketones by reaction with an alcohol is amongst the most useful protective methods,[15a–c] and the development of new procedures (reaction conditions or alcohol equivalents) is the subject of continuous efforts.[12i,15d,e] Dimethyl acetals, widely used protecting groups, have been prepared from methanol by well-established methods of homogeneous and heterogeneous catalysis.[15d] Excess of alcohol, removal of water, use of toxic or corrosive acids, high catalyst amounts, and formation of side products can be drawbacks of the reaction.

Our method presents the advantages of mild reaction conditions (at room temperature and in air) and short times; good conversions to dimethyl acetals were obtained for the aromatic 4-chlorobenzaldehyde (**7a**; Table 3, entry 1), the conjugated cinnamic aldehyde (**7b**; entry 2) the acid-sensitive thiophene-2-carbaldehyde (**7c**; entry 3), and 4-*tert*-butylcyclohexan-1-one (**7d**; entry 4) by reaction with methanol (**3f**). As expected, 4-acetylbenzaldehyde (**7e**) afforded the aldehyde dimethyl acetal **8e** in 77% yield (Table 3, entry 5).



Scheme 4 *o*-Benzenedisulfonimide-catalyzed acetal synthesis, cleavage, and interconversion

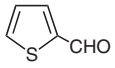
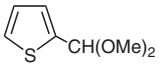
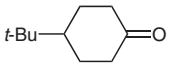
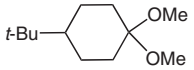
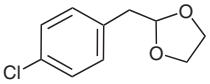
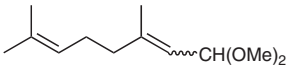
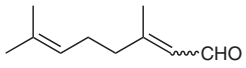
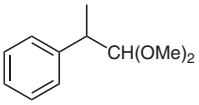
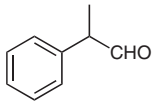
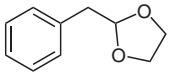
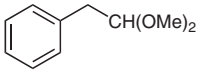
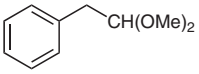
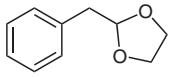
The optimal amount of catalyst **1** was 0.5–1 mol% (Table 3). Neutralization at the end of the reaction was achieved by the addition of solid sodium bicarbonate. The yields reported in Table 3 refer to pure products, isolated by flash column chromatography on silica gel deactivated by triethylamine. The acetal formation was also effected with success in solvent: from the reaction between aldehyde **7a** and ethane-1,2-diol (**9**) (**7a/9** 1:3) in toluene at

Table 2 *o*-Benzenedisulfonimide-Catalyzed Esterification Reactions[a]

Entry	Reactants		Ratio	Amount **1**	Time	Product **6**			Yield[b]
	5	**3**	**5/3**	(mol%)	(h)	**6**	R^4	R^5	(%)
1	**5a**	**3d**	1:1.1	25	1.5	**6a**	Bu	Bn	90
2	**5a**	**3e**	1:1	20	1.5	**6b**	n-C_8H_{17}	Bn	85
3	**5b**	**3c**	1:1	30	10	**6c**	Bn	CH=CHPh	40[c]
4	**5b**	**3d**	1:1.1	20	10	**6d**	Bu	CH=CHPh	37[c]
5	**5a**, **5b**	**3d**	1:1:1.1[d]	20	4	**6a** **6d**	Bu Bu	Bn CH=CHPh	89[e] 9[e]
6	**5c**	**3d**	1:1	20	3	**6e**	Bu	2-Tol	no reaction

[a] Reagents and conditions: **2**, **3**, **1**, toluene, 90 °C, time (until completion or no further progress by GC analysis).
[b] Yields refer to pure isolated products.
[c] Unchanged acid **5b** (53%, entry 3; 62%, entry 4) was recovered from the reaction mixtures.
[d] Ratio **5a/5b/3d**.
[e] Esters **6a** and **6d** were isolated partially in mixture; yields were calculated on the basis of their GC ratio and ^{1}H NMR spectra. Unchanged acids **5a** (9%) and **5b** (88%) were also recovered (quantities calculated by their ratio in ^{1}H NMR spectra).

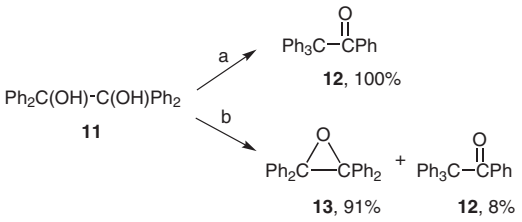
Table 3 *o*-Benzenedisulfonimide-Catalyzed Acetalization, Acetal Cleavage and Transacetalization

Entry	Reactants		Ratio	Amount	Solvent	Temp	Time	Products	Yield[a,b]
	7, **8**, or **10**	**3f** or **9**	**7/9**	**1** (mol%)		(°C)	(min)	**7**, **8**, or **10**	(%)
1	**7a** 4-ClC_6H_4CHO	**3f**	–	0.5	MeOH	r.t.	10	**8a** 4-$ClC_6H_4CH(OMe)_2$	85 (90)[c]
2	**7b** PhCH=CHCHO	**3f**	–	0.5	MeOH	r.t.	10	**8b** PhCH=CHCH$(OMe)_2$	64 (72)[c,d]
3	**7c** 	**3f**	–	0.5	MeOH	r.t.	10	**8c** 	64 (65)[c,d]
4	**7d** 	**3f**	–	0.5	MeOH	r.t.	10	**8d** 	78
5	**7e** 4-AcC_6H_4CHO	**3f**	–	0.5	MeOH	r.t.	20	**8e** 4-$AcC_6H_4CH(OMe)_2$	77
6	**7a** 4-ClC_6H_4CHO	**9**	1:3	1	toluene	90	60	**10a** 	87[d]
7	**8f** 		–	0.5	MeOH–H_2O (9:1)	r.t.	5	**7f** 	78
8	**8g** 		–	5	H_2O	70	70	**7g** 	70
9	**10b** 	**3f**	–	5	MeOH	reflux	5	**8h** 	80
10	**8h** 	**9**	1:2	5	THF	reflux	30	**10b** 	89

[a] Yields refer to pure isolated products.
[b] Products were characterized by GC-MS and ^{1}H NMR spectroscopy, and by comparison with authentic commercial samples.
[c] Yields in parentheses are of **8** obtained in the presence of **1** (1 mol%).
[d] Unchanged carbonyl compound **7** was recovered (entry 2: **7b**, 23%; entry 3: **7c**, 5%; entry 6: **7a**, 11%).

90 °C for 60 min, dioxolane derivative **10a** was isolated in 87% yield (Table 3, entry 6). *o*-Benzenedisulfonimide (**1**) also successfully catalyzed some explorative reactions of deprotection of acetals to aldehydes in alcohol–water or water (Table 3, entries 7 and 8, respectively; pure aldehydes **7f** and **7g** were isolated in good yields) and transacetalization in the reacting alcohol or in an inert solvent (Table 3, entries 9 and 10, respectively; pure dimethyl acetal **8h** and cyclic acetal **10b** were isolated in high yield).

Pinacol rearrangement in the presence of *o*-benzenedisulfonimide (**1**) was examined next (Scheme 5). The reaction of *vic*-diols is catalyzed by strong mineral acids or solid acid catalysts,[12j,k] and it has been shown that epoxides are intermediates in the rearrangement of certain diols.[16] In confirmation of this, heating of 1,1,2,2-tetraphenylethane-1,2-diol (**11**, benzopinacol) in toluene in the presence of *o*-benzenedisulfonimide (**1**) gave benzopinacolone (**12**) as the sole product (100% yield) or tetraphenyloxirane (**13**) as the main product (91% yield) (Scheme 5), the outcome depending on the reaction conditions with regard to temperature and amount of acid catalyst.



Scheme 5 *o*-Benzenedisulfonimide-catalyzed pinacol rearrangement. *Reagents and conditions*: (a) **1** (20 mol%), toluene, 110 °C, 7 h; (b) **1** (10 mol%), toluene, 90 °C, 1 h.

In conclusion, considering the ubiquitous use of strong Brønsted acids in organic synthesis and bearing in mind advantages and disadvantages of solid acid catalysts, in this work we demonstrated the synthetic usefulness of *o*-benzenedisulfonimide (**1**) in some of the most common acid-catalyzed reactions, as a nontoxic, nonvolatile, and noncorrosive recyclable acid catalyst, highly soluble in both organic solvents and water. We considered some examples of acid-catalyzed dehydrative etherification, esterification, acetalization, transacetalization, acetal cleavage, and pinacol rearrangement. The results obtained were good and showed differences in reactivity and selectivity of various substrates.

All the reactions were conducted in open-air flasks; analytical grade reagents and solvents were used, and reactions were monitored by GC and GC–MS. GC–MS data were recorded with an HP 5989B mass-selective detector connected to an HP 5890 GC cross-linked methylsilicone capillary column. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 200 spectrometer at 200 and 50 MHz, respectively, of samples in $CDCl_3$, with chemical shifts reported relative to $CDCl_3$. Column chromatography and TLC were performed on Merck silica gel 60 (70–230 mesh ASTM) and GF 254, respectively. Flash chromatography was carried out on silica gel (particle size 0.032–0.063 mm). Et_3N (1%) was always used as a mobile-phase additive to prevent deacetalization. PE (bp 40–60 °C) was used. Details of the reactions and yields for the pure (GC, GC–MS, TLC, ^{1}H NMR) isolated products are listed in Tables 1– 3. The structures and purity of all the products were confirmed by comparison of their spectral data (MS and ^{1}H NMR) with those reported in the literature or with those of available commercial samples. Commercially available reagents and solvents were purchased from Aldrich and were used without purification or distillation before use; Dowex 50X8 ion-exchange resin was purchased from Fluka. 1,3-Diphenylprop-2-en-1-ol (**4a**) and 1,3-diphenylpropan-1-ol were prepared by reduction of the commercially available 1,3-diphenylprop-2-en-1-one with $LiAlH_4$ in THF, as described in the literature.[17]

Ethers 4a–p by Etherification Catalyzed by *o*-Benzenedisulfonimide (1); General Procedures

Method A (alcohols 3a–d as solvents): *o*-Benzenedisulfonimide (**1**; 5 mol%; 0.022 g, 0.1 mmol) was added to a soln of **2** (**2a**, **2b**, or **2c**, 2.0 mmol) in alcohol **3** (**3a** or **3b**, 10 mL); the mixture was stirred at the temperature reported in Table 1. The reaction was monitored by TLC, GC, and GC–MS until complete disappearance of the starting material. The mixture was evaporated under reduced pressure and the residue was poured into Et_2O–H_2O (40 mL, 1:1). The aqueous layer was separated and the organic extract was washed with H_2O (20 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The crude residue was chromatographed on a short column; this provided products **4a**,**b**,**e**,**f**,**g**,**h**.

Method B (THF as solvent): *o*-Benzenedisulfonimide (**1**; 5 mol%; 0.022 g, 0.1 mmol) was added to a soln of **2** (**2a** or **2b**, 2.0 mmol) and **3** (**3c**, 2.0 mmol or **3d**, 4.0 mmol) in THF (10 mL), and the mixture was stirred at the temperature reported in Table 1. The reaction was monitored by TLC, GC and GC–MS; the workup was as above; this afforded pure (by GC, GC–MS, TLC, ^{1}H NMR) products **4c**,**d**,**i**.

Method C (no solvent): *o*-Benzenedisulfonimide (**1**; 5 mol%; 0.055 g, 0.25 mmol) was added to a mixture of **2** (**2b** or **2c**, 5.0 mmol) and BnOH (**3c**; 6.0 or 5.0 mmol for **2b** or **2c**, respectively), and the mixture was stirred at 60 °C in an oil bath. The reaction was monitored by GC and GC–MS; the workup was as above, and afforded pure product **4k**.

Recovery of *o*-benzenedisulfonimide (1): The aqueous layer and aqueous washings from the various reactions were collected and evaporated under reduced pressure. The residue was passed through a column of Dowex 50X8 ion-exchange resin (1.6 g resin/1 g product); elution was with H_2O. After removal of the H_2O under reduced pressure, virtually pure (by ^{1}H NMR) **1** was recovered; mp 192–194 °C (toluene) (Lit.[18] 192–194 °C).

Details of the reaction conditions and yields of products **4a–k** are listed in Table 1; chromatographic solvents and spectroscopic data are reported below for each product.

(*E*)-1,3-Diphenyl-3-ethoxyprop-1-ene (4a)[19]

Chromatography: PE–Et_2O, 6:4; colorless oil; yield: 0.37 g (77%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.33 (t, *J* = 7.0 Hz, 3 H), 3.60 (superimposed q, *J* = 7.0 Hz, 2 H diastereotopic), 4.98 (d, *J* = 6.8 Hz, 1 H), 6.38 (dd, *J* = 16.0, 6.8 Hz, 1 H), 6.68 (d, *J* = 16.0 Hz, 1 H), 7.25–7.50 (m, 10 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.72, 64.33, 82.86, 126.93 (2 C), 127.17 (2 C), 127.94, 128.00, 128.84 (4 C), 131.00, 131.45, 136.97, 141.86.

MS (EI, 70 eV): *m*/*z* (%) = 238 (70) [M$^+$], 105 (100).

(*E*)-3-Isopropoxy-1,3-diphenylprop-1-ene (4b)[20]

Chromatography: PE–Et_2O, 6:4; colorless oil; yield: 0.37 g (74%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.14 (d, *J* = 6.0 Hz, 3 H), 1.18 (d, *J* = 6 Hz, 3 H), 3.68 (app quin, *J* = 6 Hz, 1 H), 4.99 (d, *J* = 6.8 Hz, 1 H), 6.25 (dd, *J* = 15.8, 6.8 Hz, 1 H), 6.53 (d, *J* = 15.8 Hz, 1 H), 7.15–7.37 (m, 10 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.49, 22.68, 68.92, 79.81, 126.80 (2 C), 127.11 (2 C), 127.71, 127.82, 128.69 (4 C), 131.00, 131.40, 136.93, 142.22.

MS (EI, 70 eV): *m*/*z* (%) = 252 (16) [M$^+$], 105 (100).

(*E*)-3-(Benzyloxy)-1,3-diphenylprop-1-ene (4c)[21]

Chromatography: PE–Et_2O, 6:4; colorless oil; yield: 0.51 g (85%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.54 (s, 2 H), 4.98 (d, *J* = 7.0 Hz, 1 H), 6.30 (dd, *J* = 16.0, 7.0 Hz, 1 H), 6.59 (d, *J* = 16.0 Hz, 1 H), 7.17–7.43 (m, 15 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 70.43, 81.93, 126.95 (2 C), 127.33 (2 C), 127.88, 128.06 (4 C), 128.74 (2 C), 128.88 (4 C), 130.61, 131.87, 136.90, 138.76, 141.47.

MS (EI, 70 eV): *m*/*z* (%) = 300 (1) [M$^+$], 181 (100).

(*E*)-3-Butoxy-1,3-diphenylprop-1-ene (4d)[22]

Chromatography: PE–Et_2O, 9:1; colorless oil; yield: 0.37 g (70%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.2 Hz, 3 H), 1.27–1.45 (m, 2 H), 1.56–1.65 (m, 2 H), 3.31–3.53 (m, 2 H), 4.85 (d, *J* = 7.2 Hz, 1 H), 6.25 (dd, *J* = 15.8, 7.2 Hz, 1 H), 6.56 (d, *J* = 15.6 Hz, 1 H), 7.16–7.34 (m, 10 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.18, 19.67, 32.20, 68.70, 82.80, 126.79, 127.02, 127.45, 127.84, 128.68, 130.94, 131.27, 136.88, 141.81.

MS (EI, 70 eV): *m*/*z* (%) = 266 (37) [M$^+$], 105 (100).

(*E*)-3-Ethoxy-3-phenylprop-1-ene (4e)[23]

Chromatography: PE–Et_2O, 7:3; colorless oil; isolated partially in mixture with (*E*)-3-ethoxy-1-phenylprop-1-ene (**4f**); total yield: 0.18 g (56%; **4e/4f**, 1:1, by GC and ^{1}H NMR).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.20 (t, *J* = 7.0 Hz, 3 H), 3.35–3.53 (m, 2 H), 4.70 (d, *J* = 6.6 Hz, 1 H), 5.14 (d, *J* = 10.8 Hz, 1 H), 5.22 (d, *J* = 7.4, 7.2 Hz, 1 H), 5.92 (ddd, *J* = 17.0, 10.2, 6.8 Hz, 1 H), 7.22–7.32 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.53, 64.17, 83.11, 116.21, 127.01 (2 C), 127.75, 128.64 (2 C), 139.44, 141.56.

MS (EI, 70 eV): *m*/*z* (%) = 162 (60) [M$^+$], 117 (100).

(*E*)-3-Ethoxy-1-phenylprop-1-ene (4f)[23,24]

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.19 (t, *J* = 7.0 Hz, 3 H), 3.49 (q, *J* = 7.0 Hz, 2 H), 4.08 (d, *J* = 6.0 Hz, 2 H), 6.24 (dt, *J* = 15.8, 6.1 Hz, 1 H), 6.55 (d, *J* = 16.0 Hz, 1 H), 7.17–7.36 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.50, 65.90, 71.42, 126.52, 126.66 (2 C), 127.79, 128.72 (2 C), 132.40, 136.97.

MS (EI, 70 eV): *m*/*z* (%) = 162 (61) [M$^+$], 105 (100).

(*E*)-3-Isopropoxy-3-phenylprop-1-ene (4g)[25]
Chromatography: PE–Et_2O, 7:3; colorless oil; isolated partially in mixture with (*E*)-**4h**; total yield: 0.14 g (40%; **4g/4h**, 1:2, by GC and ^1H NMR).

^1H NMR (200 MHz, $CDCl_3$): δ = 1.09 (d, *J* = 6.2 Hz, 3 H), 1.14 (d, *J* = 6.2 Hz, 3 H), 3.61 (app quin, *J* = 6.2 Hz, 1 H), 4.81 (d, *J* = 6.8 Hz, 1 H), 5.10 (d, *J* = 10 Hz, 1 H), 5.17 (d, *J* = 17.8 Hz, 1 H), 5.89 (ddd, *J* = 17.0, 10.2, 6.6 Hz, 1 H), 7.21–7.30 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.30, 22.65, 68.86, 80.14, 115.88, 127.03 (2 C), 127.61, 128.56 (2C), 139.92, 142.02.

MS (EI, 70 eV): *m*/*z* (%) = 176 (7) [M^+], 117 (100).

(*E*)-1-Phenyl-3-isopropoxyprop-1-ene (4h)[26]
^1H NMR (200 MHz, $CDCl_3$): δ = 1.16 (d, *J* = 6.0 Hz, 6 H), 3.64 (app quin, *J* = 6.2 Hz, 1 H), 4.09 (d, *J* = 6.0 Hz, 2 H), 6.26 (dt, *J* = 15.8, 5.8 Hz, 1 H), 6.55 (d, *J* = 16.0 Hz,1 H), 7.17–7.36 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.35 (2 C), 68.93, 71.16, 126.66 (2 C), 127.06, 127.72, 128.70 (2 C), 131.96, 137.07.

MS (EI, 70 eV): *m*/*z* (%) = 176 (28) [M^+], 105 (100).

(*E*)-3-Butoxy-3-phenylprop-1-ene (4i)[27]
Chromatography: PE–Et_2O, 9:1; colorless oil; isolated partially in mixture with (*E*)-**4j**; total yield: 0.19 g (50%; **4i/4j**, 1:2, by GC and ^1H NMR).

^1H NMR (200 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 7.0 Hz, 3 H), 1.26–1.44 (m, 2 H), 1.49–1.62 (m, 2 H), 3.27–3.45 (m, 2 H), 4.67 (d, *J* = 6.6 Hz, 1 H), 5.13 (d, *J* = 11.0 Hz, 1 H), 5.20 (d, *J* = 18.4 Hz, 1 H), 5.90 (ddd, *J* = 17.0, 10.4, 6.6 Hz, 1 H), 7.20–7.30 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.16, 19.64, 32.16, 68.63, 83.17, 116.31, 126.98 (2 C), 127.68, 128.59 (2 C), 139.50, 141.65.

MS (EI, 70 eV): *m*/*z* (%) = 190 (23) [M^+], 117 (100).

(*E*)-3-Butoxy-1-phenylprop-1-ene (4j)[28]
^1H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.2 Hz, 3 H), 1.26–1.44 (m, 2 H), 1.49–1.63 (m, 2 H), 3.43 (t, *J* = 6.6 Hz, 2 H), 4.07 (d, *J* = 5.8 Hz, 2 H), 6.24 (dt, *J* = 15.8, 6.0 Hz, 1 H), 6.55 (d, *J* = 15.8 Hz, 1 H), 7.15–7.36 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.17, 19.59, 32.09, 70.45, 71.62, 126.66 (3 C), 127.78, 128.73 (2 C), 132.28, 136.99.

MS (EI, 70 eV): *m*/*z* (%) = 190 (40) [M^+], 105 (100).

(*E*)-3-(Benzyloxy)-1-phenylprop-1-ene (4k)[29]
Chromatography: PE–Et_2O, 9:1; colorless oil; yield: 0.67 g (60%).

^1H NMR (200 MHz, $CDCl_3$): δ = 4.17 (dd, *J* = 6.0, 1.4 Hz, 2 H), 4.55 (s, 2 H), 6.30 (dt, *J* = 16.0, 6.0 Hz, 1 H), 6.61 (d, *J* = 16.0 Hz, 1 H), 7.18–7.39 (m, 10 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 70.99, 72.40, 126.30, 126.73, 127.90, 128.04, 128.66, 128.79, 132.75, 136.95, 138.50.

MS (EI, 70 eV): *m*/*z* (%) = 224 (1) [M^+], 180 (59), 105 (100), 91 (89).

3-(Benzyloxy)cyclohex-1-ene (4l)[29]
Chromatography: PE–Et_2O, 9.5:0.5; colorless oil; yield: 0.71 g (75%).

^1H NMR (200 MHz, $CDCl_3$): δ = 1.46–1.96 (m, 6 H), 3.88–3.92 (m, 1 H), 4.48 and 4.56 (2 d, *J* = 12 Hz, 2 H diastereotopic), 5.72–5.86 (m, 2 H), 7.20–7.30 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.49, 25.46, 28.58, 70.23, 72.39, 127.61, 127.84 (2 C), 128.00, 128.53 (2 C), 131.15, 139.29.

MS (EI, 70 eV): *m*/*z* (%) = 188 (10) [M^+], 97 (45), 91 (100).

3-Butoxycyclohex-1-ene (4m)[30]
Chromatography: PE–Et_2O, 9.8:0.2; colorless oil; yield: 0.24 g (31%).

^1H NMR (200 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 7.2 Hz, 3 H), 1.25–1.80 (m, 8 H), 1.8–1.95 (m, 2 H), 3.34–3.49 (m, 2 H), 3.71–3.77 (m, 1 H), 5.70–5.80 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.13, 19.49, 19.62, 25.43, 28.53, 32.50, 68.20, 72.92, 128.28, 130.71.

MS (EI, 70 eV): *m*/*z* (%) = 154 (5) [M^+], 81 (100).

Bis(cyclohex-2-en-1-yl) Ether (4p)[31]
Isolated as byproduct by flash chromatography of the crude mixture of the reaction of Table 1, entry 14; NMR spectra are consistent with a mixture of the two enantiomers and the mesoform.

Yield: 0.08 g (18%).

^1H NMR (200 MHz, $CDCl_3$): δ = 1.36–2.09 (m, 12 H), 3.90–4.00 (m, 2 H), 5.60–5.79 (m, 4 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.44, 19.72, 25.40, 29.39, 29.84, 70.73, 70.78, 128.90, 129.04, 130.51, 130.58.

MS (EI, 70 eV): *m*/*z* (%) = 178 (5) [M^+], 81 (100).

2-Methyl-4-(octyloxy)but-2-ene (4n)[32]
Chromatography: PE–Et_2O, 9.8:0.2; colorless oil; isolated in mixture with **4o** (**4n/4o**, 40:60, by GC); total yield: 0.40 g (40%; **4n/4o**, 1:1.3, by GC and ^1H NMR).

^1H NMR (200 MHz, $CDCl_3$): δ = 0.78–0.84 (m; **4n** and **4o**), 1.07–1.30 (m; **4n** and **4o**), 1.36–1.55 (m; **4n** and **4o**), 1.61 and 1.68 (2 s, 6 H; **4n**), 3.20 (t, *J* = 6.7 Hz, 2 H; **4o**), 3.33 (t, *J* = 6.6 Hz, 2 H; **4n**), 3.87 (d, *J* = 6.6 Hz, 2 H; **4n**), 5.02 (d, *J* = 10.8 Hz, 1 H; **4o**), 5.04 (d, *J* = 18.4 Hz, 1 H; **4o**), 5.20–5.32 (m, 1 H; **4n**), 5.76 (dd, *J* = 17.6, 10.8 Hz, 1 H; **4o**).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.30, 22.85, 26.05 (2 C), 26.41, 29.50, 29.69, 30.80, 32.03, 62.85, 67.41, 70.59, 74.94, 113.50, 121.60, 144.59.

MS (EI, 70 eV): *m*/*z* (%) = 198 (10) [M^+], 183 (20), 71 (100).

3-Methyl-3-(octyloxy)but-1-ene (4o)
Isolated as pure product and partially in mixture with **4n**.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.78–0.84 (m, 3 H), 1.08–1.30 (m, 14 H), 1.36–1.56 (m, 4 H), 3.20 (t, *J* = 6.7 Hz, 2 H), 5.02 (d, *J* = 10.8 Hz, 1 H), 5.04 (d, *J* = 18.4 Hz, 1 H), 5.76 (dd, *J* = 17.6, 10.8 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.29, 22.85, 26.05 (2 C), 26.41, 29.48, 29.69, 30.78, 32.04, 62.85, 74.94, 113.52, 144.58.

MS (EI, 70 eV): *m*/*z* (%) = 198 (10) [M^+], 183 (48), 71 (100).

Selective Etherification of 1,3-Diphenylprop-2-en-1-ol (2a) with Benzyl Alcohol (3c) in the Presence of 1,3-Diphenylpropan-1-ol
According to the conditions of Method B, *o*-benzenedisulfonimide (**1**; 5 mol%; 0.022 g, 0.1 mmol) was added to a soln of **2a** (0.42 g, 2.0 mmol), 1,3-diphenylpropan-1-ol (0.43 g, 2.0 mmol), and BnOH (**3c**; 0.22 g, 2.0 mmol) in THF (10 mL), and the mixture was stirred at r.t. for 30 min. After the usual workup of the reaction mixture, the crude residue was chromatographed on a short column (PE–Et_2O, 6:4); this provided pure **4c** (0.54 g, 90%) and unchanged 1,3-diphenylpropan-1-ol (quantitative).

Esters 6a–d by Esterification Catalyzed by *o*-Benzenedisulfonimide (1); General Procedure
o-Benzenedisulfonimide (**1**; 25 mol%; 0.11 g, 0.5 mmol) was added to a soln of **5** (**5a** or **5b**, 2 mmol) and alcohol **3** (**3c**, **3d**, or **3e**; 2 or 2.2 mmol) in toluene (10 mL), and the mixture was stirred at 90 °C

for 30 min. The mixture was evaporated under reduced pressure and the residue was poured into Et_2O–H_2O (40 mL, 1:1). The aqueous layer was separated and the organic extract was washed with H_2O (20 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The aqueous layer and aqueous washings were collected, evaporated under reduced pressure, and passed through a column of Dowex 50X8 ion-exchange resin to recover pure **1**. The crude residue was chromatographed on a short column (silica gel, PE–Et_2O, 8:2); this provided pure compounds **6**. Details of the reactions and yields of products **6a–e** are listed in Table 2; spectroscopic data are reported below for each product.

Butyl Phenylacetate (6a)[33]
Colorless oil; yield: 0.38 g (90%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 7.0 Hz, 3 H), 1.23–1.34 (m, 2 H), 1.48–1.58 (m, 2 H), 3.56 (s, 2 H), 4.04 (t, *J* = 6.6 Hz, 2 H), 7.15–7.28 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.86, 19.27, 30.80, 41.66, 64.94, 127.21, 128.72 (2 C), 129.43 (2 C), 134.40, 171.88.

MS (EI, 70 eV): *m*/*z* (%) = 192 (5) [M$^+$], 91 (100).

Octyl Phenylacetate (6b)[33]
Colorless oil; yield: 0.42 g (85%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.80–0.86 (m, 3 H), 1.12–1.21 (m, 10 H), 1.52–1.60 (m, 2 H), 3.56 (s, 2 H), 4.03 (t, *J* = 7.0 Hz, 2 H), 7.14–7.24 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.29, 22.84, 26.03, 28.76, 29.36 (2 C), 31.96, 41.69, 65.23, 127.21, 128.72 (2 C), 129.44 (2 C), 134.42, 171.88.

MS (EI, 70 eV): *m*/*z* (%) = 248 (5) [M$^+$], 91 (100).

Benzyl Cinnamate (6c)[34]
After completion of the reaction, unchanged cinnamic acid (**5b**) was separated by washing of the organic extracts with 5% aq NaOH. Usual workup of the organic phase and chromatographic purification gave product **6c**. The basic washings were acidified with 35% HCl and then extracted with Et_2O; after evaporation of the solvent, pure acid **5b** (by GC, GC–MS, ^{1}H NMR) was recovered; yield: 0.14 g (53%).

Product 6c
Yield: 0.19 g (40%); white solid; mp 36–36.8 °C (PE) (Lit.[31] 38–39 °C).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.20 (s, 2 H), 6.44 (d, *J* = 16.0 Hz, 1 H), 7.31–7.34 (m, 8 H), 7.40–7.48 (m, 2 H), 7.68 (d, *J* = 16.0 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 66.57, 118.08, 128.31 (2 C), 128.48 (4 C), 128.80, 129.10 (2 C), 130.55, 134.56, 136.26, 145.39, 167.00.

MS (EI, 70 eV): *m*/*z* (%) = 238 (25) [M$^+$], 131 (100).

Butyl Cinnamate (6d)[35]
Unchanged cinnamic acid **5b** was recovered as described above.

Product 6d
Colorless oil; yield: 0.15 g (37%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.3 Hz, 3 H), 1.38 (app sext, *J* = 7.3 Hz, 2 H), 1.63 (app quin, *J* = 6.9 Hz, 2 H), 4.15 (t, *J* = 6.6 Hz, 2 H), 6.38 (d, *J* = 16.0 Hz, 1 H), 7.30–7.33 (m, 3 H), 7.44–7.49 (m, 2 H), 7.62 (d, *J* = 16.0 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.96, 19.40, 30.97, 64.63, 118.47, 128.24 (2 C), 129.06 (2 C), 130.40, 134.66, 144.75, 167.31.

MS (EI, 70 eV): *m*/*z* (%) = 204 (20) [M$^+$], 131 (100).

Selective Esterification of Phenylacetic Acid (5a) with Butan-1-ol (3d) in the Presence of Cinnamic Acid (5b) (Table 2, entry 5)
o-Benzenedisulfonimide (**1**; 20 mol%; 0.09 g, 0.4 mmol) was added to a soln of **5a** (0.27 g, 2 mmol), **5b** (0.30 g, 2 mmol), and **3d** (0.16 g, 2.2 mmol) in toluene (10 mL), and the mixture was stirred at 90 °C for 4 h (GC analyses showed no more progress of the reaction). The workup was as described above. Esters **6a** and **6d** were obtained partially in mixture after purification by column chromatography; yields were calculated from their GC ratio and ^{1}H NMR spectra. Unchanged acids **5a** and **5b** were recovered as described above; yields were calculated from their ratio in ^{1}H NMR spectra.

Acetal Synthesis, Cleavage, and Interconversion Catalyzed by *o*-Benzenedisulfonimide (1); Typical Procedures
Thiophene-2-carbaldehyde Dimethyl Acetal (8c) (Table 3, entry 3)
o-Benzenedisulfonimide (**1**; 0.5 mol%; 0.0022 g, 0.01 mmol) was added to a soln of **7c** (0.22 g, 2 mmol) in MeOH (**3f**; 5 mL), and the mixture was stirred at r.t. for 10 min. The mixture was treated with solid $NaHCO_3$ and evaporated under reduced pressure and the residue was poured into Et_2O–H_2O (40 mL, 1:1). The organic extract was dried (Na_2SO_4) and evaporated under reduced pressure. The crude residue was chromatographed on a short column (silica gel deactivated by Et_3N, PE–Et_2O, 9.5:0.5); this provided pure (by GC, GC–MS, TLC, ^{1}H NMR) **8c**.

Yield: 0.20 g (64%); colorless oil.[36]

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.30 (s, 6 H), 5.58 (s, 1 H), 6.93–6.97 (m, 1 H), 7.00–7.03 (m, 1 H), 7.24 (d, *J* = 5.0 Hz,1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 52.73 (2 C), 100.28, 125.63, 125.89, 126.87, 141.72.

MS (EI, 70 eV): *m*/*z* (%) = 158 (8) [M$^+$], 127 (100).

4-Chlorobenzaldehyde Ethylene Acetal (10a) (Table 3, entry 6)
o-Benzenedisulfonimide (**1**; 1 mol%; 0.0044 g, 0.02 mmol) was added to a soln of **7a** (0.28 g, 2 mmol) and **9** (0.37 g, 6 mmol) in toluene (5 mL), and the mixture was stirred at 90 °C for 60 min. After the usual workup, the crude residue was chromatographed on a short column (PE–Et_2O, 9.5:0.5).

Yield: 0.32 g (87%); colorless oil.[37]

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.92–3.99 (m, 2 H), 4.02–4.09 (m, 2 H), 5.72 (s, 1 H), 7.29 (d, *J* = 8.8 Hz, 2 H), 7.36 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 65.51 (2 C), 103.21, 128.10 (2 C), 128.75 (2 C), 135.20, 136.69.

MS (EI, 70 eV): *m*/*z* (%) = 184 (35) [M$^+$], 183 (100).

Citral (7f) (Table 3, entry 7)
o-Benzenedisulfonimide (**1**; 0.5 mol%; 0.0022 g, 0.01 mmol) was added to a soln of **8f** (0.40 g, 2 mmol) in MeOH–H_2O (5 mL, 9:1), and the mixture was stirred at r.t. for 5 min. After the usual workup, the crude residue was chromatographed on a short column (PE–Et_2O, 9.5:0.5); this provided pure **7f**, whose spectral data were identical to those of a commercially available sample.

Yield: 0.26 g (80%); colorless oil.

Phenylacetaldehyde Dimethyl Acetal (8h) (Table 3, entry 9)
o-Benzenedisulfonimide (**1**; 5 mol%; 0.022 g, 0.1 mmol) was added to a soln of **10b** (0.33 g, 2 mmol) in MeOH (10 mL), and the mixture was stirred at reflux for 5 min. After the usual workup, the crude residue was chromatographed on a short column (PE–Et_2O, 9.5:0.5); this provided pure **8h**, whose spectral data were identical to those of a commercially available sample.

Yield: 0.26 g (80%); colorless oil.

Phenylacetaldehyde Ethylene Acetal (10b) (Table 3, entry 10)
o-Benzenedisulfonimide (**1**; 5 mol%; 0.022 g, 0.1 mmol) was added to a soln of **8h** (0.33 g, 2 mmol) and **9** (0.12 g, 4 mmol) in THF (5 mL), and the mixture was stirred at reflux for 30 min. After the usual workup, the crude residue was chromatographed on a short column (PE–Et_2O, 9.5:0.5); this provided pure **10b**, whose spectral data were identical to those of a commercially available sample.

Yield: 0.29 g (89%); colorless oil.

Details of the reactions and yields of products **7f**,**g**, **8a**–**e**,**h**, and **10a**,**b** are listed in Table 3. Chromatography for all the products: PE–Et_2O, 9.5:0.5. The structures and purity of the products **7f**,**g**, **8a**,**h**, and **10a**,**b** were confirmed by comparison of their spectral data (MS and ^1H NMR) with those of commercially available samples of analytical purity (Aldrich).

Cinnamaldehyde Dimethyl Acetal (8b)[15d,38]
Colorless oil; yield: 0.23 g (64%).

^1H NMR (200 MHz, $CDCl_3$): δ = 3.32 (s, 6 H), 4.91 (d, *J* = 4.2 Hz, 1 H), 6.10 (dd, *J* = 16.2, 4.8 Hz, 1 H), 6.67 (d, *J* = 16.2 Hz, 1 H), 7.20–7.37 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 52.93 (2 C), 103.11, 125.90, 126.94 (2 C), 127.80 (2 C), 128.32, 133.79, 136.29.

MS (EI, 70 eV): *m*/*z* (%) = 178 (30) [M^+], 147 (100).

4-*tert*-Butylcyclohexanone Dimethyl Acetal (8d)[15d,36]
Colorless needles; yield: 0.31 g (78%); mp 38–39 °C (pentane) (Lit.[39] 38 °C).

^1H NMR (200 MHz, $CDCl_3$): δ = 0.78 (s, 9 H), 0.90–1.25 (m, 5 H), 1.54–1.61 (m, 2 H), 1.96–2.01 (m, 2 H), 3.08 (s, 3 H), 3.13 (s, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.79 (3 C), 27.85 (2 C), 32.48, 32.97 (2 C), 47.57, 47.77 (2 C), 100.08.

MS (EI, 70 eV): *m*/*z* (%) = 200 (5) [M^+], 101 (100).

4-Acetylbenzaldehyde Dimethyl Acetal (8e)[36]
Colorless oil; yield: 0.30 g (77%).

IR (CCl_4): 1691 (CO) cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.52 (s, 3 H), 3.24 (s, 6 H), 5.36 (s, 1 H), 7.47 (d, *J* = 8.0 Hz, 2 H), 7.87 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.86, 52.83, 102.44, 127.17 (2 C), 128.43 (2 C), 137.26, 143.26, 198.01.

MS (EI, 70 eV): *m*/*z* (%) = 194 (3) [M^+], 163 (100).

Phenyl Triphenylmethyl Ketone (12, Benzopinacolone)[40] by Pinacol Rearrangement
o-Benzenedisulfonimide (**1**; 20 mol%; 0.066 g, 0.3 mmol) was added to a soln of **11** (0.55 g, 1.5 mmol) in toluene (10 mL), and the mixture was stirred at 110 °C for 7 h. The reaction was monitored by TLC, GC, and GC–MS analyses until complete conversion into the desired product. The mixture was poured into Et_2O–H_2O (40 mL, 1:1), the aqueous layer was separated, and the organic extract was washed with H_2O (20 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The crude residue was purified by flash chromatography (PE–Et_2O, 9:1) to provide pure **12**.

Yield: 0.52 g (100%); white solid; mp 182.5–183.2 °C (toluene–PE) (Lit.[41] 185–187 °C).

^1H NMR (200 MHz, $CDCl_3$): δ = 7.09–7.24 (m, 18 H), 7.59–7.63 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 71.2, 126.87 (3 C), 127.80 (2 C), 127.99 (6 C), 131.10 (6 C), 131.25 (2 C), 131.88, 137.66, 143.39 (3 C), 199.03.

IR (CCl_4): 1684 (CO) cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 332 [M^+ – 16], 243 (100).

Tetraphenyloxirane (13)[42] by Pinacol Rearrangement
o-Benzenedisulfonimide (**1**; 10 mol%; 0.033 g, 0.15 mmol) was added to a soln of **11** (0.55 g, 1.5 mmol) in toluene (10 mL), and the mixture was stirred at 90 °C for 2 h. The reaction was monitored by TLC, GC, and GC–MS analyses until complete disappearance of **11**. After the usual workup, purification of the crude residue by flash chromatography (PE–CH_2Cl_2, 8:2) yielded pure **13**; yield: 0.46 g (91%); and rearranged product **12**; yield: 0.04 g (8%).

Product 13
Colorless needles; mp 211.1–212.0 °C (toluene–PE) (Lit.[38] 211–213 °C).

^1H NMR (200 MHz, $CDCl_3$): δ = 7.03–7.09 (m, 10 H), 7.11–7.20 (m, 8 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 74.03 (2 C), 127.26 (4 C), 127.76 (8 C), 128.42 (8 C), 138.79 (4 C).

MS (EI, 70 eV): *m*/*z* (%) = 348 (40) [M^+], 165 (100).

Acknowledgment

This work was supported by the Italian MIUR and by the Università degli Studi di Torino.

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