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o-Benzenedisulfonimide as a Reusable Brønsted Acid Catalyst for Ritter-Type Reactions

Margherita Barbero,[a] Stefano Bazzi,[a] Silvano Cadamuro,[a] and Stefano Dughera*[a]

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Reactions between various benzyl alcohols or *tert*-butyl alcohol and nitriles were carried out in the presence of catalytic amounts (usually 10–20 mol-%) of *o*-benzenedisulfonimide as a Brønsted acid catalyst; the reaction conditions were mild and the yields of amides were good. The catalyst was easily recovered and purified, ready to be used in further reactions, with economic and ecological advantages.

Introduction

We have recently[1] reported the use of *o*-benzenedisulfonimide (**1**) in catalytic amounts as a Brønsted acid in some acid-catalyzed organic reactions such as etherification, esterification and acetalization under very mild and selective conditions. The catalyst was easily recovered and purified, ready to be used in further reactions, with economic and ecological advantages.

o-Benzenedisulfonimide (**1**, Figure 1) has a high acidity (pK_a –4.1 at 20 °C)[2] and was described for the first time in 1921 and 1926;[3] however, modified procedures of its synthesis have been proposed more recently.[4] The key intermediate for its preparation is *o*-benzenedisulfonyl chloride, which is now commercially available. Very recently, *o*-benzenedisulfonimide itself has also become commercially available.

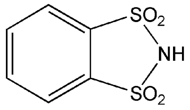

Figure 1. *o*-Benzenedisulfonimide (**1**).

In 1948, Ritter and co-workers reported the efficient synthesis of amides through the reactions between alkenes and many nitriles in the presence of sulfuric acid.[5] Over the years, mainly alcohols have also come to be used in place of alkenes,[6] and several methodologies have very recently been employed for Ritter reactions in which sulfuric acid is replaced variously by 2,4-dinitrobenzenedisulfonic acid[7a] as a Brønsted acid or other protic acids,[7b–7e] Lewis acids,[8] metal complexes,[9] solid-supported acids,[10] and many others.[11] The main disadvantages of these methods are often the use of toxic, corrosive, and expensive catalysts, and their recovery and reuse is often impossible.

In this paper we wish to report a comprehensive study of the reactions between various alcohols and nitriles in the presence of catalytic amount of **1** to provide amides in Ritter fashion.

Results and Discussion

To begin with, we studied the reaction between diphenylmethanol (**2a**, Scheme 1) and MeCN (**3a**) in the presence of catalytic amounts of **1** (10 mol-%). The reaction was carried out in the presence of an excess of **3a** as solvent and proceeded under mild conditions. *N*-(Diphenylmethyl)acetamide (**4a**) was obtained in high yield (89%; Table 1, Entry 1). On monitoring of the progress of this reaction by GC-MS, the formation of bis(diphenylmethyl) ether (**5a**) was also observed; however, the quantity of **5a** diminished in the course of the reaction, and the compound had completely disappeared after 8 h. On the other hand, we were able to isolate and characterize **5a** on stopping the reaction after 2 h.

Furthermore, **1** was recovered in excellent yield (86%), simply on concentrating the aqueous layer and washings under reduced pressure as reported in the Experimental Section. The recovered **1** was reused as catalyst in other two consecutive reactions between **2a** and **3a**. The results are listed in Table 1: the reaction times increased in the course of the different reactions, but the yields of **4a** and the recovery of **1** were always good.

In light of the above, we think that the reaction proceeds through the catalytic cycle[7a] described in Scheme 2, in which the interaction between **2a** and **1** generates the prod-

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[a] Dipartimento di Chimica Generale e Chimica Organica dell'Università di Torino,
Corso M. d'Azeglio 48, 10125 Torino, Italy
Fax: +39-011-6707642
E-mail: stefano.dughera@unito.it

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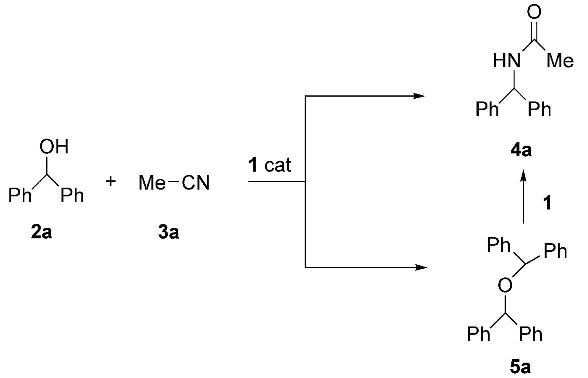


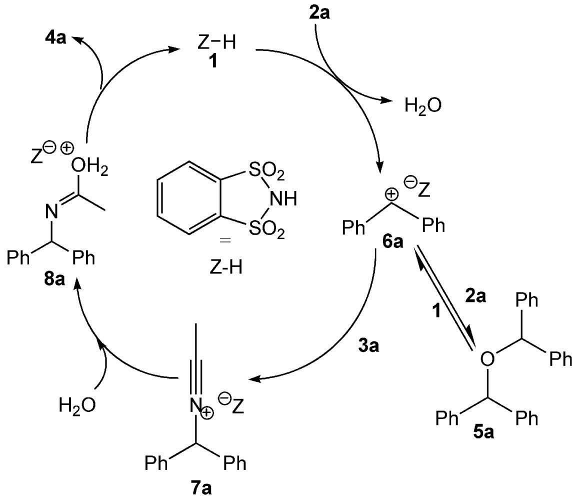
Scheme 1. Reactions between **2a** and **3a**.

Table 1. Consecutive reactions with recycled **1**.

Entry	Time [h]	Yield (%) of **4a**[a]	Recovery (%) of **1**
1	8	89[b]	86,[c] 0.19 g
2	15	84[d,e]	89,[f] 0.17 g
3	24	84[g,h]	100, 0.17 g

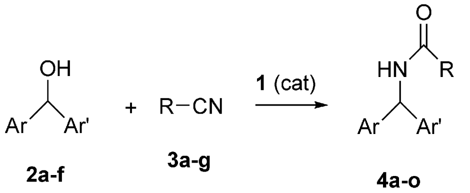
[a] Yields refer to the pure products. [b] The reaction was performed with **2a** (10 mmol, 1.84 g) and **1** (10 mol-%, 0.22 g, 1 mmol). [c] The recovered **1** was reused in Entry 2. [d] The reaction was performed with **2a** (8.7 mmol, 1.60 g) and **1** (10 mol-%, 0.19 g, 0.87 mmol). [e] **2a** (0.10 g, 6%) was also recovered. [f] The recovered **1** was reused in Entry 3. [g] The reaction was performed with **2a** (7.76 mmol, 1.43 g) and **1** (10 mol-%, 0.17 g, 0.77 mmol). [h] **2a** (0.11 g, 8%) was also recovered.

uct **6a**. This, reacting with **3a**, gives rise to compound **7a**, which undergoes a nucleophilic attack by the water produced in the first step. In this manner, through the intermediate **8a**, **4a** is formed, with regeneration of **1**, ready to start another catalytic cycle. Note that **6a**, reacting with **2a**, furnishes **5a**, regenerating **6a**.



Scheme 2. Catalytic cycle.

On these grounds, alcohols **2a**–**f** were treated with nitriles **3a**–**g**, either aliphatics or aromatics (Scheme 3), in the presence of catalytic amounts of **1** (10 mol-%) in order to synthesize amides **4a**–**o** under easy and mild conditions (Method A). Also worthy of note is the importance of these compounds in biological and medical fields[7a] and their use as protecting groups.[7a] The results, reported in Table 2, allow the following conclusions to be drawn. Either with aliphatic (**3a**, **3g**) or aromatic (**3b**, **3d**–**f**) substrates the result obtained were good, independently of any electronic effects of the groups on an aromatic ring (Table 2, Entries 1, 3, 6, 8, 10, 12). In contrast, steric effects were important: with regard to **3c**, the presence of a methyl group in the *ortho* position drastically reduced the yield (Table 2, Entry 5).



2	Ar	Ar'
a	Ph	Ph
b	Ph	4-$MeOC_6H_4$
c	Ph	4-$NO_2C_6H_4$
d	4-FC_6H_4	4-FC_6H_4
e	4MeO-C_6H_4	4-$MeOC_6H_4$
f	2,4,6-$Me_3C_6H_2$	2,4,6-$Me_3C_6H_2$

3	R
a	Me
b	Ph
c	2-MeC_6H_4
d	3-MeC_6H_4
e	4-MeC_6H_4
f	4-$MeCOC_6H_4$
g	CH_2=CH

4	Ar	Ar'	R
a	Ph	Ph	Me
b	Ph	Ph	Ph
c	Ph	Ph	2-MeC_6H_4
d	Ph	Ph	3-MeC_6H_4
e	Ph	Ph	4-MeC_6H_4
f	Ph	Ph	4-$MeOC_6H_4$
g	Ph	Ph	CH_2=CH

4	Ar	Ar'	R
h	Ph	4-$MeOC_6H_4$	Me
i	Ph	4-$MeOC_6H_4$	Ph
j	Ph	4-$NO_2C_6H_4$	Me
k	Ph	4-$NO_2C_6H_4$	Ph
l	4-FC_6H_4	4-FC_6H_4	Me
m	4-FC_6H_4	4-FC_6H_4	Ph
n	4-$MeOC_6H_4$	4-$MeOC_6H_4$	Me
o	2,4,6-$Me_3C_6H_2$	2,4,6-$Me_3C_6H_2$	Me

Scheme 3. Reactions between alcohols **2** and nitriles **3**.

Furthermore, with respect to compounds **2**, electronics effects were fundamental. In particular, on treatment of **2e** (bearing two electron-donating groups) with **3a**, no traces of **4n** were detected, but bis(4-methoxyphenyl)methane and 4,4′-dimethoxybenzophenone were recovered (Table 2, Entry 26). It is known from the literature[12] that diarylmethyl isopropyl ethers, under catalytic acid conditions, undergo disproportionation reactions with selective hydride transfer to the more electrophilic bis-benzylic carbon centres and with the formation of the corresponding diarylmethanes and acetone. Under our conditions, ether **5n** was able to react in the same way, most probably due to the presence of two methoxy groups. With **5b**, bearing only one methoxy group, however, no disproportionation reaction occurred

Table 2. Synthesis of amides **4** from alcohols **2** and nitriles **3**.

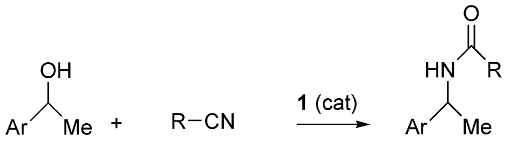
Entry	Reactants	Method	Time [h]	Temp. [°C]	Yields (%)[a,b]
1	**2a**, **3a**	A	8	reflux	**4a**, 89[c]
2	**2a**, **3a**	B	24	75	**4a**, 94[d]
3	**2a**, **3b**	A	7	100	**4b**, 87[e]
4	**2a**, **3b**	B	16	100	**4b**, 87[d]
5	**2a**, **3c**	A	30	100	**4c**, 30[f]
6	**2a**, **3d**	A	24	100	**4d**, 74[d]
7	**2a**, **3d**	B	48	100	**4d**,76[d]
8	**2a**, **3e**	A	24	100	**4e**, 80
9	**2a**, **3e**	B	48	100	**4e**, 74[d]
10	**2a**, **3f**	A	48	reflux	**4f**, 73
11	**2a**, **3f**	B	84	75	**4f**, 75[d]
12	**2a**, **3g**	A	24	reflux	**4g**, 99
13	**2a**, **3g**	B	48	75	**4g**, 81[d]
14	**2b**, **3a**	A	5	reflux	**4h**, 85
15	**2b**, **3a**	B	16	75	**4h**, 80[d]
16	**2b**, **3b**	A	3	100	**4i**, 77
17	**2b**, **3b**	B	16	100	**4i**, 79[d]
18	**2c**, **3a**	A	24	reflux	**4j**, 97[d, g]
19	**2c**, **3a**	B	40	75	**4j**, 88[d,h]
20	**2c**, **3b**	A	8	100	**4k**, 80[h]
21	**2c**, **3b**	B	24	100	**4k**, 77[d,h]
22	**2d**, **3a**	A	5	reflux	**4l**, 97[d]
23	**2d**, **3a**	B	16	75	**4l**, 91[d]
24	**2d**, **3b**	A	5	100	**4m**, 98
25	**2d**, **3b**	B	12	100	**4m**, 87[d]
26	**2e**, **3a**	A	2	reflux	**4n**,–[i]
27	**2f**, **3a**	A	24	75	**4o**, 51[j]

[a] Yields refer to the pure products. [b] The presence of ethers **5** was always detected by GC-MS analysis in all the reactions with the exception of Entry 26; compounds **5** disappeared during the reactions. [c] The reaction was also performed with **1** (100 mol-%, 2.19 g, 10 mmol). No traces of the possible *N*-diphenylmethyl-*o*-benzenedisulfonimide were detected. [d] The crude residues were amides **4** in a virtually pure state. No columns were necessary to purify the products. [e] The crude residue was washed with pentane (10 mL) in a Buchner funnel to afford pure **4b**. [f] Ether **5a** {MS (EI): m/z = 350 [M]$^+$} and **2a** {MS (EI): m/z = 184 [M]$^+$} were both detected in the GC-MS analyses of the crude residue. However, it was not possible to obtain them pure. [g] The reaction was performed with **1** (20 mol-%, 0.44 g, 2 mmol). With **1** (10 mol-%, 0.22 g, 1 mol) the reaction time was 48 h and the yield of **4j** was 88% (2.77 g). [h] The reaction was performed with **1** (20 mol-%, 0.44 g, 2 mmol). [i] No traces of amide **4n** were detected. Bis(4-methoxyphenyl)methane (0.95 g, 42% yield), and 4,4′-dimethoxybenzophenone (1.41 g, 58% yield) were isolated from a flash column (eluent: petroleum ether/ethyl acetate, 9:1). [j] Bis(2,4,6-trimethylphenyl)methane {MS (EI): m/z = 252 [M]$^+$} and bis(2,4,6-trimethylphenyl)methanone {MS (EI): m/z = 266 [M]$^+$} were detected in the GC-MS$^+$ analyses of the crude residue. However, it was not possible to obtain them pure.

(Table 2, Entries 14, 16). In contrast, in the presence of electron-withdrawing groups (Table 2, Entries 18, 20) the reactions were considerably slower, but the yields of **4j** and **4k** were always good. Moreover, it seems that methyl groups in the *ortho* positions (**2f**) caused a decrease in the yield of **4o** (Table 2, Entry 27). However, the low amounts were due to the same side-reaction (disproportionation) as described before (Table 2, Entry 26). In fact, GC-MS analyses showed the presence of the corresponding diarylmethane and ketone.

It is interesting to remark that the reactions could also be carried out under solvent-free conditions (Method B; Table 2, Entries 2, 4, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25), in which the nitriles **3** were used in stoichiometric amounts relative to alcohols **2**. The reactions were usually slower, but the yields were always good, with evident economic and ecological advantages.

To explore the synthetic usefulness of *o*-benzenedisulfonimide (**1**) in Ritter-type reactions further, we also investigated three other types of alcohols besides alcohols **2**. We first studied the reactions between 1-arylethanols **9a–e** and nitriles **3a** and **3b** (Scheme 4); the results are listed in Table 3. It should be noted that traces of corresponding vinylbenzenes were always detected by GC-MS; obviously, their origin was due to the competitive elimination. Good yields of amides **10** were usually obtained (Table 3, Entries 1–3, 5), but even in this case the electronic effects of the substituents on the aromatic rings of **9** were very important. In fact, on treatment of **9c** (bearing a methoxy group in the *para* position) with **3a**, no traces of **10d** were detected. The only product was 1,3-bis(4-methoxyphenyl)but-1-ene (Table 3, Entry 4). In contrast, when the methoxy group was in the *meta* position (**9b**, Table 3, Entry 3), **10c** was isolated after a short reaction time.



9a-e **3a,b** **10a-f**

9	Ar
a	Ph
b	3-MeOC$_6$H$_4$
c	4-MeOC$_6$H$_4$
d	4-ClC$_6$H$_4$
e	4-NO$_2$C$_6$H$_4$

3	R
a	Me
b	Ph

10	Ar	R
a	Ph	Me
b	Ph	Ph
c	3-MeOC$_6$H$_4$	Me
d	4-MeOC$_6$H$_4$	Me
e	4-ClC$_6$H$_4$	Me
f	4-NO$_2$C$_6$H$_4$	Me

Scheme 4. Reactions between alcohols **9** and nitriles **3**.

Probably there is a greater delocalization of the positive charge of the carbocation when the methoxy group is situated in the *para* position, and for this reason the latter is less available to nucleophilic attack by **3a**.

On these grounds, the elimination reaction happens preferentially, and the resulting 4-methoxystyrene, reacting with 1-(4-methoxyphenyl)ethyl cation, furnishes 1,3-bis(4-methoxyphenyl)but-1-ene. On the other hand, when the methoxy group is situated in the *meta* position, because the positive charge of the carbocation is less delocalized, the latter is easily attacked by **3a**, with the formation of **10c**. In the presence of electron-withdrawing groups (Table 3, Entry 6) the reaction was slowed down so much that only traces of **10f** were detected.

Next, reactions between *tert*-butyl alcohol (**11**) and nitriles **3a–c**, **3e** and **3h** were examined (Scheme 5) and the results are reported in Table 4. This reaction is useful to prepare bulky amides, which may be hydrolysed to provide hindered amines.[9a]

Table 3. Synthesis of amides **10** from alcohols **9** and nitriles **3**.

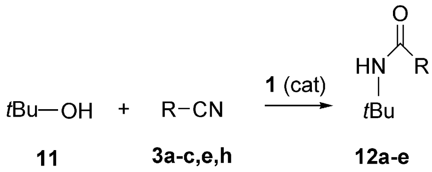
Entry	Reactants	Time [h]	Temp. [°C]	Yields (%)[a,b]
1	**9a**, **3a**	48	reflux	**10a**, 93[c,d]
2	**9a**, **3b**	8	100	**10b**, 94[e]
3	**9b**, **3a**	15	reflux	**10c**, 63[f]
4	**9c**, **3a**	0.5	reflux	**10d**, –[g]
5	**9d**, **3a**	27	reflux	**10e**, 72
6	**9e**, **3a**	96	reflux	**10f**, traces[h]

[a] Yields refer to the pure products. [b] Traces of styrenes and the presence of bis(diarylethyl) ethers were always detected by GC-MS in all the reactions with the exceptions of Entries 4 and 6; the ethers disappeared during the reactions. [c] The reaction time was only 24 h and the yield of **10a** was 83% (1.35 g) in the presence of **1** (20 mol-%, 0.44 g, 2 mmol). [d] The reaction was also performed with **1** (100 mol-%, 2.19 g, 10 mmol). No traces of the possible *N*-(1-phenylethyl)-*o*-benzenedisulfomide were detected. [e] After 48 h at reflux, with **1** (20 mol-%, 0.44 g, 2 mmol) and equimolar amounts of reactants **9a** and **3b** (10 mmol, 1.22 g and 10 mmol, 1.03 g respectively) the reaction was not complete. [f] The reaction was performed with **1** (20 mol-%, 0.44 g, 2 mmol). [g] No traces of amide **10d** were detected. 1,3-Bis(4-methoxyphenyl)but-1-ene (0.72 g, 53% yield) was isolated from a flash column (eluent: petroleum ether/ethyl acetate, 9:1). [h] On GC-MS analyses, besides the predominant **9e** {MS (EI): *m*/*z* = 167 [M]$^+$}, only traces of amide **10f** {MS (EI): *m*/*z* = 208 [M]$^+$} were detected, also in the presence of **1** (20 mol-%, 0.44 g, 2 mmol).

Table 4. Synthesis of amides **12** from alcohol **11** and nitriles **3**.

Entry	Reactant	Temp. [°C]	Yields (%)[a,b]
1	**3a**	reflux	**12a**, 83[c]
2	**3b**	100	**12b**, 80[d,e,f]
3	**3c**	100	**12c**, traces[g]
4	**3e**	100	**12d**, 77[h]
5	**3h**	reflux	**12e**, 56

[a] Yields refer to the pure products. [b] No traces of the possible di-*tert*-butyl ether were detected. [c] The reaction was performed with **3a** (10 mmol, 0.41 g) and an excess of **11** (5 mL) at reflux for 72 h. Compound **11** was evaporated under reduced pressure and the crude residue was filtered on a short flash column, with elution with petroleum ether/ethyl acetate (9:1) to provide pure amide **12a**. [d] When the reaction was performed with equimolar amounts of reactants **3b** and **11** (10 mmol, 1.03 g and 10 mmol, 0.74 g respectively), only traces of **12b** were detected by GC-MS after 48 h. [e] The reactions was also performed with **3b** (10 mmol, 0.41 g) and an excess of **11** (5 mL) at reflux for 20 h. The usual workup furnished **12b** (1.26 g, 73% yields). [f] When the reaction was performed with **1** (10 mol-%, 0.22 g, 1 mmol), only traces of **12b** were detected after 48 h by GC-MS. [g] Only traces of **12c** {MS (EI): *m*/*z* = 191 [M]$^+$} were detectable by GC-MS after 48 h. [h] Because **12d** decomposed on the chromatography column, the reaction was performed with an excess of **11** (5 mL), **3e** (10 mmol, 0.41 g) and **1** (40 mol-%, 0.88 g, 4 mmol) at reflux for 72 h. The usual workup furnished **12d** (1.47 g, 77% yield) virtually pure. When the reaction was performed with **1** (20 mol-%, 0.44 g, 0.2 mol) the reaction time was longer (168 h) and the yield of **12d** was lower (1.05 g, 56%).

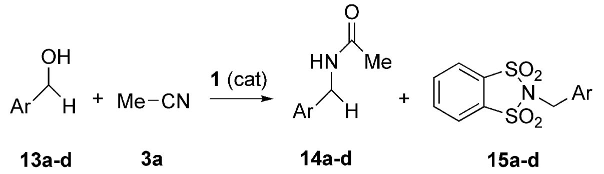


3	R	12	R
a	Me	a	Me
b	Ph	b	Ph
c	2-MeC$_6$H$_4$	c	2-MeC$_6$H$_4$
e	4-MeC$_6$H$_4$	d	4-MeC$_6$H$_4$
h	*n*Pr	e	*n*Pr

Scheme 5. Reactions between alcohol **11** and nitriles **3**.

The yields of amides **12** were usually satisfactory, with the exception of the bulky **3c** (Table 4, Entry 4), for which steric effects became important. However, it must be stressed that use of 20 mol-% amounts of catalyst **1** was necessary for the completion of all the reactions.

Finally, we studied the behaviour of benzyl alcohols **13a**–**d** (Scheme 6), and the results, reported in Table 5, were clearly less positive. First of all, with 10 or 20 mol-% amount of catalyst **1** no traces of amide **14b** were detected (Table 5, Entries 3, 4). It was necessary to increase the amount of **1** to 40 mol-% (Table 5, Entries 1, 5) or 100 mol-% (Table 5, Entries 1, 2, 5, 6) to obtain **14a** or **14b** in moderate yields. However, it must be stressed that, despite the large amounts of **1** required, it was at least recovered in excellent yield (80%). Moreover, besides **14a** and **14b**, *N*-benzyl-*o*-benzenedisulfonimides **15a** and **15b** were also isolated (Table 5, Entries 3–6). The formation of the latter compounds was very surprising. The anion of **1** is a poor nucleophile[4a] and in our prior research[1] we have never detected the presence of possible *N*-substituted *o*-benzenedisulfonimides. Moreover, in our previous paper[13] we described the preparation of arenediazonium *o*-benezenedisulfonimides, by diazotization of aromatic amines with isopentyl nitrite in the presence of **1**.



13,14,15	Ar
a	Ph
b	4-MeC$_6$H$_4$
c	4-MeOC$_6$H$_4$
d	4-NO$_2$C$_6$H$_4$

Scheme 6. Reactions between alcohols **13** and compound **3a**.

An X-ray analysis of one of these arenediazonium *o*-benezenedisulfonimide confirmed its ionic nature. This article[13] also reports that the thermal decomposition of these salts results in two products, one of which is the result of loss of nitrogen and aryl attack at the nitrogen atom of **1**.

Possibly the formation of **15** occurs on heating of **13** with stoichiometric amounts of **1**, in spite of the poor nucleophilicity. Moreover, no traces of possible *N*-substituted *o*-benzenedisulfonimides were detected when **2a** or **9a** were allowed to react in the presence of a 100 mol-% quantity of **1**. In this last case, it is possible that the greater steric hindrance of **2** and **9** could prevent the formation of *N*-substituted *o*-benzenedisulfonimides. On treatment of **13c** with **3a** a not negligible amount of bis(4-methoxyphenyl)methane was also recovered (Table 5, Entry 7). The formation of this

Table 5. Synthesis of amides **14** from alcohols **13** and compound **3a**.

Entry	Reactant	Amount (%) of **1**	Time [h]	Yields (%)[a]	
1	**13a**	40	96	**14a**, 30[b]	**15a**, 35
2	**13a**	100	48	**14a**, 35[c]	**15a**, 28
3	**13b**	10	48	**14b**, –[d]	**15b**, –
4	**13b**	20	48	**14b**, –[d]	**15b**, –
5	**13b**	40	48	**14b**, 51[e]	**15b**, 30
6	**13b**	100	24	**14b**, 64[f]	**15b**, 29
7	**13c**	20	48	**14c**, 60[g]	**15c**, –
8	**13d**	100	72	**14d**, –[h]	**15d**, –

[a] Yields refer to the pure products. [b] Dibenzyl ether (0.03 g, 15% yield) was also isolated. [c] The presence of dibenzyl ether was also detected by GC-MS, but it disappeared during the reaction. [d] After 48 h, only unreacted **13b** was detectable by GC-MS. [e] Bis(4-methylbenzyl) ether (0.03 g, 13% yield) was also isolated. [f] The presence of bis(4-methylbenzyl) ether was also detected by GC-MS, but it disappeared during the reaction. [g] Bis(4-methoxyphenyl)methane (0.09 g, 40% yield) was also isolated. [h] No traces of **14d** or **15d** were detected by GC-MS analysis. 4-Nitrobenzyl acetate (0.11 g, 31% yield) was isolated.

by-product was astonishing, but it could be assumed that an electrophilic aromatic substitution had occurred, with the 4-methoxybenzyl cation, reacting with **13c**, replacing the CH_2OH group, which leaves as protonated formaldehyde. On the other hand, the presence of a strongly electron-withdrawing group (Table 5, Entry 8) prevented the formation of **14d**. The only product obtained was 4-nitrobenzyl acetate, originating from the nucleophilic addition of **13d** to **3a** and the hydrolysis of the adduct formed.

Conclusions

In this paper the synthetic usefulness of *o*-benzenedisulfonimide (**1**) as a catalyst in Ritter-type reactions has been demonstrated. The target products **4a–o**, **10a–f** and **12a–e** were obtained in good to excellent yields (average yields were 81%, 64% and 59%, respectively), while less satisfactory results were obtained for **14a–d** (average yield was 40%). Furthermore, in comparison with strong liquid or solid Brønsted acids, extensively used for research laboratories to chemical manufacturing plants, **1** turned out be a safe, non-volatile, and non-corrosive catalyst. A further valuable aspect of the use of **1** is its high solubility in both organic solvents and water. In particular, its easy recovery in high yield from the reaction mixture, due to its complete solubility in water, and its reuse without loss of catalytic activity in other reactions, is very important, offering economic and ecological advantages.

Experimental Section

General Remarks: All reactions were conducted in flasks open to the air; analytical grade reagents and solvents were used and reactions were monitored by TLC, GC and GC-MS. Mass spectra were recorded with an HP 5989B mass selective detector connected to an HP 5890 GC cross-linked methyl silicone capillary column. 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 the hydrolysis of amides. Petroleum ether (PE) refers to the fraction boiling in the 40–70 °C range. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker Avance 200 spectrometer at 200 and 50 MHz, respectively. *o*-Benzenedisulfonimide (**1**) was prepared as reported in the literature;[13] alcohols **2d–f**, **9c** and **9e** were prepared by reduction of commercially available by Aldrich benzophenones or acetophenones with $LiAlH_4$ or $NaBH_4$, as described in the literature.[14] All the other alcohols (**2**, **9**, **11**, **13**) and all the nitriles **3** were purchased from Aldrich or Fluka. Yields of the pure (GC, GC-MS, TLC, ^1H NMR, ^{13}C NMR) isolated amides **4**, **10**, **12** and **14** are reported in Tables 2, 3, 4, and 5, respectively. Structures and purities of all the products obtained in this research were confirmed by comparison of their physical (m.p.) and spectroscopic data with those reported in the literature. Satisfactory microanalyses were obtained for all new compounds.

***N*-(Diarylmethyl)amides 4. General Procedures. Method A (Nitrile as Solvent):** *o*-Benzenedisulfonimide (**1**, 10 mol-%, 0.22 g, 1 mmol) was added to a solution of an alcohol **2** (10 mmol) in a nitrile **3** (5 mL) and the mixture was stirred at the temperature reported in Table 2. The reactions were monitored by TLC, GC and GC-MS until the complete disappearance of the alcohols **2** and the ethers **6**; the reactions time are reported in Table 2. The reaction mixture was poured into dichloromethane/water (100 mL, 1:1). The aqueous layer was separated and extracted with dichloromethane (2 × 50 mL). The combined organic extracts were washed with water (2 × 50 mL), dried with Na_2SO_4 and concentrated under reduced pressure. The crude residues were chromatographed on a short flash column, with elution with petroleum ether/ethyl acetate (9:1) to provide pure amides **4**. The aqueous layer and aqueous washings were collected and evaporated under reduced pressure. After removal of the water, virtually pure (^1H NMR) *o*-benzenedisulfonimide (**1**) was recovered (about 80% yields in all the reactions) m.p. 192–194 °C (toluene, ref.[13] m.p. 192–194 °C).

The recovered **1** was employed in other two catalytic cycles with **2a** and **3a** under the conditions described above; Table 1 reports the yields of amide **4a**, the yields of recovered **1** and the reaction times.

***N*-(Diphenylmethyl-)-3-toluamide (4d):** M.p. 158 °C (MeOH), ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 7.62–7.59$ (m, 4 H), 7.45–7.25 (m, 10 H), 6.72–6.64 (m, 1 H), 6.46 (d, $J = 7.60$ Hz, 1 H), 2.41 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): $\delta = 166.9$, 141.7, 138.7, 134.4, 132.6, 128.9, 128.6, 128.0, 127.7, 124.2, 57.5, 21.5 ppm. MS (EI): $m/z = 301$ $[M]^+$. $C_{21}H_{19}NO$ (301.39): calcd. C 83.69, H 6.35, N 4.65; found C 83.73, H 6.31, N 4.65.

4-Acetyl-*N*-(diphenylmethyl)benzamide (4f): M.p. 183 °C (MeOH), ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 7.97$ and 7.91 (2 d, 1:1, $J = 8.20$ Hz, 4 H), 7.45–7.24 (m, 10 H), 6.79–6.76 (m, 1 H), 6.46 (d, $J = 7.60$ Hz, 1 H), 2.64 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): $\delta = 197.0$, 165.9, 141.3, 138.3, 132.7, 128.9, 128.7, 127.9, 127.8, 57.8, 27.0 ppm. MS (EI): m/z (%) = 329 $[M]^+$. $C_{22}H_{19}NO_2$ (329.40): calcd. C 80.22, H 5.81, N 4.25; found C 80.25, H 5.86, N 4.26.

***N*-[(4-Nitrophenyl)phenylmethyl]benzamide (4k):** M.p. 169–170 °C (MeOH), ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 8.17$ and 7.82 (2 d, 1:1, $J = 8.60$ Hz, 4 H), 7.67–7.25 (m, 10 H), 6.91–6.87 (m, 1 H), 6.47 (d, $J = 7.60$ Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): $\delta = 167.0$, 149.0, 147.2, 140.2, 133.7, 133.0, 129.4, 128.8, 128.3, 127.9, 127.7, 127.3, 124.0, 57.5 ppm. MS (EI): $m/z = 332$ $[M]^+$. $C_{20}H_{16}N_2O_3$ (332.36): calcd. C 72.28, H 4.85, N 8.43; found C 72.29, H 4.88, N 8.44.

N-[Bis(4-fluorophenyl)methyl]benzamide (4m): M.p. 177–179 °C (MeOH), ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.81–7.78 (m, 2 H), 7.56–7.38 (m, 3 H), 7.27–7.20 (m, 4 H), 7.10–6.98 (m, 4 H), 6.85–6.81 (m, 1 H), 6.38 (d, J = 7.60 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 166.8, 162.3 (d, $^1J_{C,F}$ = 244.5 Hz), 137.3 (d, $^4J_{C,F}$ = 3.1 Hz), 134.1, 132.1, 129.2 (d, $^3J_{C,F}$ = 8.1 Hz), 128.8, 127.2, 115.8 (d, $^2J_{C,F}$ = 21.3 Hz), 56.37 ppm. MS (EI): *m*/*z* = 323 [M]$^+$. $C_{20}H_{15}F_2NO$ (323.34): calcd. C 74.29, H 4.68, F 11.75, N 4.33; found C 74.27, H 4.68, F 11.74, N 4.37.

In a collateral verification, **1** (10 mol-%, 0.22 g, 1 mmol) was added to a solution of **2a** (1.84 g, 10 mmol) in **3a** (5 mL) and the mixture was stirred at reflux for 2 h. TLC, GC and GC-MS analyses showed the presence of three product: **2a**, **4a** and ether **5a**. The reaction was stopped, and the usual workup furnished a crude residue that was chromatographed on a short flash column with elution with petroleum ether/ethyl acetate (9:1). The first eluted product was bis(diphenylmethyl) ether (**5a**, 0.73 g, 41% yield); the second was **2a** (0.13 g, 7% yield) and the third was **4a** (1.02 g, 46% yield).

Method B (without Solvent): *o*-Benzenedisulfonimide (**1**, 10 mol-%, 0.22 g, 1 mmol) was added to a mixture of alcohols **2** (10 mmol) and nitriles **3** (10 mmol) and the reactions were monitored by TLC, GC and GC-MS until the complete disappearance of **2** and ethers **5**; the reaction times are reported in Table 2. The above workup furnished crude residues that were virtually pure amides **4**. Virtually pure (^{1}H NMR) *o*-benzenedisulfonimide (**1**) was also recovered (about 80% yield in all the reactions).

***N*-(1-Arylethyl)amides 10. General Procedure:** *o*-Benzenedisulfonimide (**1**, 10 mol-%, 0.22 g, 1 mmol) was added to a solution of alcohols **9** (10 mmol) in nitriles **3** (5 mL) according to the conditions reported above, and the mixture was stirred at the temperature reported in Table 3. The reactions were monitored by TLC, GC and GC-MS until the complete disappearance of **9** and the corresponding bis(arylethyl) ethers; the reaction times are reported in Table 3. The usual workup provided crude residues that were chromatographed on a short flash column, with elution with petroleum ether/ethyl acetate (9:1) to provide pure amides **10**.

Virtually pure (^{1}H NMR) *o*-benzenedisulfonimide (**1**) was also recovered (about 80% yield in all the reactions).

In a collateral verification, *o*-benzenedisulfonimide (**1**, 10 mol-%, 0.22 g, 1 mmol) was added to a solution of **9a** (1.22 g, 10 mmol) in **3a** (5 mL) and the mixture was stirred at reflux for 8 h. TLC, GC and GC-MS analyses showed the presence of three products: traces of styrene {MS (EI): *m*/*z* = 104 [M]$^+$}, bis(1-phenylethyl) ether and amide **10a**. The reaction was stopped, and the usual workup furnished a crude residue that was chromatographed on a short flash column with elution with petroleum ether/ethyl acetate (9:1). The first eluted product was bis(1-diphenylethyl) ether [colourless oil (ref.[27] oil), mixture about 1:1 (from GC and ^{1}H NMR) of the *meso* form and of the two enantiomers (0.08 g, 7% yield)], and the second was amide **10a** (1.02 g, 63% yield).

***N*-*tert*-Butylamides 12. General Procedure:** *o*-Benzenedisulfonimide (**1**, 20 mol-%, 0.44 g, 2 mmol) was added to a solution of *tert*-butyl alcohol (**11**, 0.74 g, 10 mmol) in a nitrile **3** (5 mL) under the conditions given above and the mixture was stirred at the temperature reported in Table 4 for 48 h. No traces of the possible di-*tert*-butyl ether were detected. The usual workup provided crude residues that were chromatographed on a short flash column with elution with petroleum ether/ethyl acetate (9:1) to provide pure amides **12**.

After removal of the water under reduced pressure, virtually pure (^{1}H NMR) *o*-benzenedisulfonimide (**1**) was recovered (about 80% yield in all reactions).

***N*-Benzylamides 14. General Procedure:** *o*-Benzenedisulfonimide (**1**) was added to a solution of a benzyl alcohol **13** (2.0 mmol) in **3a** (5 mL) under the conditions given above; the catalyst amounts are reported in Table 5. The mixture was stirred at reflux at the time reported in Table 4. TLC, GC and GC-MS analyses showed the presence of two main products, amides **14** and *N*-benzyl-*o*-benzenedisulfonimides **15**, besides small amounts of the dibenzyl ethers. The usual workup provided crude residues that were chromatographed on short flash columns with elution with petroleum ether/diethyl ether (1:1). The first eluted products were *N*-benzyl-*o*-benzenedisulfonimides **15**; the second were amides **14**. After removal of the water under reduced pressure, virtually pure (^{1}H NMR) *o*-benzenedisulfonimide (**1**) was recovered (about 80% yield in all the reactions).

***N*-(4-Methylbenzyl)-*o*-benzenedisulfonimide (15b):** M.p. 111–112 °C (toluene), ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.08–7.97 and 7.93–7.87 (2 m, 1:1, 4 H), 7.43 and 7.22 (2 d, 1:1, J = 7.80 Hz, 4 H), 4.86 (s, 2 H), 2.37 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 138.7, 135.6, 135.0, 130.4, 129.8, 128.5, 122.5, 45.5, 21.4 ppm. MS (EI): *m*/*z* = 323 [M]$^+$. $C_{14}H_{13}NO_4S_2$ (323.38): calcd. C 52.00, H 4.05, N 4.33, S 19.83; found C 52.03, H 4.09, N 4.35, S 19.82.

Supporting Information (see also the footnote on the first page of this article): Spectroscopic and characterization data of known products.

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