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# Arenediazonium *o*-benzenedisulfonimides as efficient reagents for Heck-type arylation reactions

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**Abstract**—Arenediazonium *o*-benzenedisulfonimides can be used as new and efficient reagents for Heck-type arylation reactions of some common substrates containing C–C multiple bonds, namely ethyl acrylate, acrylic acid, acroleyne, styrene and cyclopentene. The reactions were carried out in an organic solvent, in the presence of $Pd(OAc)_2$ as pre-catalyst, and gave rise to arylated products, for example, ethyl cinnamates, cinnamic acids, cinnamic aldehydes and stilbenes, possessing an (*E*)-configuration, and 1-arylcyclopentenes, in good to excellent yields. It is noteworthy that all the reactions led to the recovery, in greater than 80% yield, of *o*-benzenedisulfonimide, recyclable for the preparation of other diazonium salts.


## 1. Introduction

As part of a broader project aimed at exploring the synthetic potential of a family of arenediazonium salts that are stable in the dry state, that is, the arenediazonium *o*-benzenedisulfonimides **1**,[1a,b] in this paper we have focused our attention on the reactivity of the said salts **1** as electrophilic reagents in Heck-type carbon–carbon coupling reactions.

Since 1970 through to the present day, the palladium-catalyzed arylation of olefins, activated or not, by aryl halides or triflates (the Heck reaction), has undergone wide development,[2] not only on the laboratory scale but also on the industrial scale for fine chemical production.[3]

The first electrophiles alternative to halides and triflates, tested in Heck-type coupling reactions, were the arenediazonium salts.[2–4] Further studies, especially over the past 15 years, have led to a marked increase in the synthetic value of diazonium salts in Heck-type reactions, compared with that of conventional reagents.[5,6] Indeed, there are many advantages associated with diazonium salts, particularly the greater reactivity of these salts, due to the fact that the diazonium group is a better nucleofuge than the halide or triflate:[5e,f,j] (a) the reactions do not require a base, or additional ligands, whose addition instead leads to uncontrolled decomposition of the salts themselves; (b) diazonium salts function under mild temperature conditions and for this reason are also suitable for reactions with thermally labile olefins; (c) reaction times are usually short; (d) coupling products are always obtained in high yields; (e) there is the possibility of aqueous one-pot procedures (tandem diazotization—Heck reactions) starting directly from the anilines;[4a,5j,6e] (f) the wide and ready availability of the starting compounds, that is, anilines, compared with the corresponding halides or triflates.

It has been demonstrated that the Heck-type reactions of arenediazonium salts are highly dependent on the nature of the diazonium counter-anion.[5g] The most commonly used salts are, by far, the tetrafluoroborates and, more recently, also the trifluoroacetates.[5b] However, it has been reported that perchlorates and fluorides also give good results, while, instead, halides and sulphates are totally inefficient for the Heck reactions.

Our present work highlights that dry arenediazonium *o*-benzenedisulfonimides **1** are a useful alternative to arenediazonium tetrafluoroborates in Heck-type carbon–carbon coupling reactions.

## 2. Results and discussion

A few years ago,[1] we reported that salts **1** can be prepared easily in excellent yields, by diazotization of primary aromatic amines with *i*-pentyl nitrite in the presence of *o*-benzenedisulfonimide (**6**), in glacial acetic acid or formic acid, at 0–10 °C. These salts, which are easily isolated in

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the dry state, show excellent stability at rt, and can therefore be kept safely, ready for use, for an unlimited time.

In the study described herein, a great variety of salts **1** in the dry state were reacted with some of the more common substrates used in the Heck reactions, for example, ethyl acrylate (**2**), acrylic acid (**3**), acroleyne (**4**), styrene (**5**) and cyclopentene (**11**), to give the corresponding arylation products, and therefore, ethyl cinnamates **7**, cinnamic acids **8**, cinnamic aldehydes **9**, stilbenes **10**, possessing an (*E*)-configuration, and 1-arylcyclopentenes **12** (Schemes 1 and 2). All reactions were carried out in an organic solvent, in the presence of $Pd(OAc)_2$, 1 mol% with respect to the reacting salt **1**, as the pre-catalyst. Note that in the present work we did not test any other catalyst/pre-catalyst different from $Pd(OAc)_2$. As already reported in the literature for other diazonium salts, also in these reactions no ligands were necessary; only in the case of acrylic acid (**3**) and acroleyne (**4**) it was necessary to work in the presence of an inorganic base. Tables 1–3 show the working conditions and the results of the reactions.

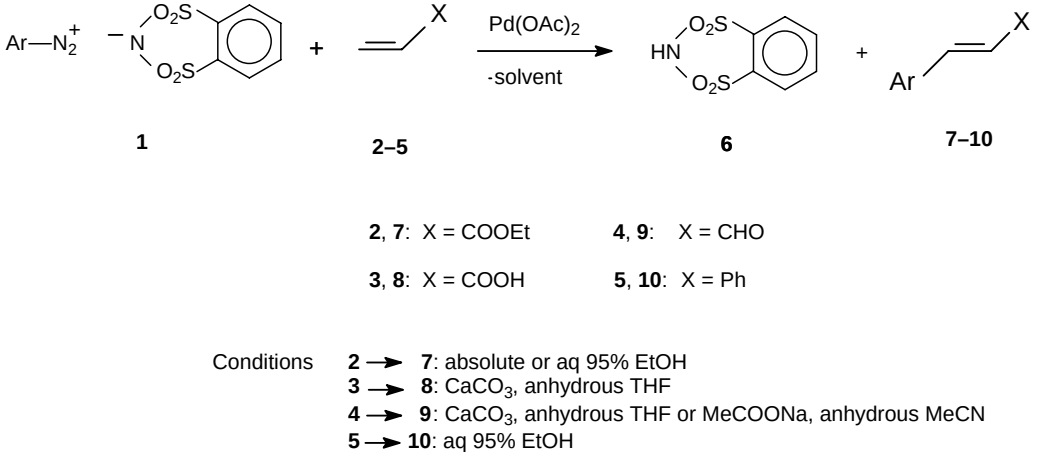
It is important to underline that all the reactions led to the recovery, in greater than 80% yield, of *o*-benzenedisulfonimide (**6**), recyclable for the preparation of other salts **1**.

### 2.1. Heck-type arylation of ethyl acrylate (2) with dry arenediazonium *o*-benzenedisulfonimides 1 to give (*E*)-ethyl cinnamates 7a–o

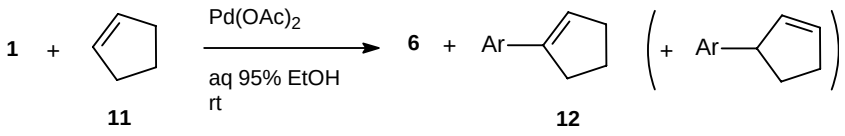
Cinnamic esters are compounds that are important industrially as UV absorbers, antioxidants in plastics and as key intermediates and starting materials in the synthesis of a great variety of pharmaceuticals, agrochemicals and fragrances.[7] Numerous methods for their preparation can be found in the literature. However, on an industrial scale, cinnamic esters are usually produced via Perkin and Claisen condensations of the corresponding aromatic aldehydes.[7b,8] An alternative and convenient synthesis of this class of compounds is the Heck arylation of acrylic esters with aryl halides.[2a] Such a reaction is also used on an industrial scale, for example, to prepare the most common UV-B sunscreen, namely 2-ethylhexyl 4-methoxycinnamate.[3]

It has been proposed that, instead of aryl halides in the Heck arylation to prepare cinnamic esters, arenediazonium salts could also be used,[4–6] mainly tetrafluoroborates, as such, or generated in situ starting from triazenes[5g,i] or anilines,[4a,c,6e] in the presence or absence of bases and with various palladium catalysts. As an alternative to the tetrafluoroborates, trifluoroacetates[5b] have also been proposed. Recently, (*E*)-cinnamic esters were also prepared by means of tandem Heck-esterification reactions, starting from arenediazonium tetrafluoroborates and acrylic acid in alcoholic solvents.[5h,6g]

In this work, numerous salts **1**, variously substituted, were reacted with ethyl acrylate (**2**), in a molar ratio of 1:1.2, in the presence of $Pd(OAc)_2$ (1 mol% with respect to salt **1**), as pre-catalyst. Two procedures for the preparation of ethyl cinnamates **7** were developed. The results can be found in Table 1. In procedure A the reactions were carried out in absolute EtOH, usually at 70 °C, and reached completion in short times of between 5 and 60 min (with the sole exception of entry 19 of Table 1, that required 2 h). Reaction completion was indicated by a negative test of azocoupling with 2-naphthol. Instead, in procedure B, the reactions were carried out in 95% aqueous EtOH at rt (20–25 °C) and the reaction times were much longer, varying from 30 min to 50 h. Both procedures proved to be general in that they gave positive results in the presence of both electron-withdrawing and electron-donating groups




**Scheme 1.** Heck-type arylation of ethyl acrylate (**2**), acrylic acid (**3**), acroleyne (**4**) and styrene (**5**).




**Scheme 2.** Heck-type arylation of cyclopentene (**11**).

**Table 1**. Ethyl cinnamates **7a–o**

| Entry no. | Starting compound **1** | Ar in **1**, **7** | Procedure | *T* (°C) | Reaction time (min) | Product **7** | Yield (%)[a] | Yield (%) lit.[b] |
|---|---|---|---|---|---|---|---|---|
| 1 | **1a** | 2-$MeC_6H_4$ | A | 70 | 5 | **7a** | 70 | 75–100[5g,6b] |
| 2 | | | B | rt | 5 h | | 74 | |
| 3 | **1b** | 4-$MeC_6H_4$ | A | 70 | 30 | **7b** | 84 | 78–99[4c,5b,g,6b] |
| 4 | | | B | rt | 2.5 h | | 95 | |
| 5 | **1c** | 2-$MeOC_6H_4$ | A | 70 | 15 | **7c** | 78[c] | 75–97[5g,i,j] |
| 6 | | | A | rt | 90 | | 84 | |
| 7 | | | B | rt | 60 | | 90 | |
| 8 | **1d** | 3-$MeOC_6H_4$ | A | 70 | 15 | **7d** | 29[d] | |
| 9 | | | A | rt | 15 h | | 74 | |
| 10 | | | B | rt | 6 h | | 59 | |
| 11 | **1e** | 4-$MeOC_6H_4$ | A | 70 | 40 | **7e** | 84 | 68–98[5g–j] |
| 12 | | | B | rt | 4 h | | 78 | |
| 13 | **1f** | 4-$ClC_6H_4$ | A | 70 | 15 | **7f** | 89 | 69–92[5h–j] |
| 14 | | | B | rt | 30 | | 89 | |
| 15 | **1g** | 3-$BrC_6H_4$ | A | 70 | 15 | **7g** | 87 | |
| 16 | | | B | rt | 30 h[e] | | tr[f] | |
| 17 | **1h** | 4-$BrC_6H_4$ | A | 70 | 60 | **7h** | 92 | 78–84[5g,j] |
| 18 | | | B | rt | 30 | | 92 | |
| 19 | **1i** | 4-$IC_6H_4$ | A | 70 | 2 h | **7i** | 76 | |
| 20 | | | B | rt | 1.5 h | | 76 | |
| 21 | **1j** | 2-$NO_2C_6H_4$ | A | 70 | 15 | **7j** | 93 | |
| 22 | | | B | rt | 30 | | 88 | |
| 23 | **1k** | 4-$NO_2C_6H_4$ | A | 70 | 5 | **7k** | 97 | 45–95[5b,6b] |
| 24 | | | B | rt | 15 | | 100 | |
| 25 | **1l** | 2-$HOOCC_6H_4$ | A | 70 | 45 | **7l** | 74 | 65[5j] |
| 26 | | | B | rt | 5 h | | 88 | |
| 27 | **1m** | 4-$CNC_6H_4$ | A | 70 | 30 | **7m** | 73 | |
| 28 | | | A | rt | 17 h | | 97 | |
| 29 | | | B | rt | 51 h | | 42 | |
| 30 | **1n** | 2,4-$(NO_2)_2C_6H_3$ | A | 70 | 15 | **7n** | 80[g] | |
| 31 | | | B | rt | 2.5 h | | 80[g] | |
| 32 | **1o** | 2-MeOCO-3-thienyl | A | 70 | 15 | **7o** | 81[h] | |
| 33 | | | B | rt | 18 h | | 89 | |

[a] Yield of pure product after column chromatography.
[b] Range of yields reported in the literature, starting from tetrafluoroborates or trifluoroacetates.
[c] Ethyl 3,3-bis(2-methoxyphenyl)-2-propenoate was also isolated in 19% yield (0.09 g): MS *m/z* 312 ($M^+$); $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 1.34 (t, $J=7.1$ Hz, 3H), 3.70 (s, 6H), 4.29 (q, $J=7.1$ Hz, 2H), 6.45 (s,1H), 6.81–7.45 (m, 8H).
[d] Ethyl 3-methoxyphenyl ether was also isolated in 31% yield (0.07 g): MS *m/z* 152 ($M^+$).
[e] A test of azo coupling with 2-naphthol was still positive.
[f] tr=traces.
[g] 1,3-Dinitrobenzene was also isolated in 16% yield (0.07 g): MS *m/z* 168 ($M^+$).
[h] 2-Methoxycarbonylthiophene was also isolated in 10% yield (0.02 g): MS *m/z* 142 ($M^+$).

**Table 2**. Cinnamic acids **8a–d**, cinnamic aldehydes **9a–e** and stilbenes **10a–c**

| Entry no. | Starting compound **1** | Ar in **1**, **8–10** | X in **3–5**, **8–10** | Solvent | Base | *T* (°C) | Reaction time (h) | Product **8–10** | Yield (%)[a] | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | **8** | **9** | **10** |
| 1 | **1b** | 4-$MeC_6H_4$ | COOH | THF | $CaCO_3$ | 60 | 12 | **8a** | 93 | | |
| 2 | **1e** | 4-$MeOC_6H_4$ | COOH | THF | $CaCO_3$ | 60 | 48[b] | **8b** | 59 | | |
| 3 | | | | MeCN | MeCOONa | 60 | 6 | | 67 | | |
| 4 | **1f** | 4-$ClC_6H_4$ | COOH | THF | $CaCO_3$ | 60 | 4.5 | **8c** | 96 | | |
| 5 | **1k** | 4-$NO_2C_6H_4$ | COOH | THF | $CaCO_3$ | 40 | 3.5 | **8d** | 55 | | |
| 6 | **1b** | 4-$MeC_6H_4$ | CHO | THF | $CaCO_3$ | 40 | 4.5 | **9a** | | 95 | |
| 7 | **1e** | 4-$MeOC_6H_4$ | CHO | THF | $CaCO_3$ | 40 | 26[b] | **9b** | | tr[c] | |
| 8 | | | | MeCN | MeCOONa | rt | 3 | | | 83 | |
| 9 | **1f** | 4-$ClC_6H_4$ | CHO | THF | $CaCO_3$ | 40 | 1.5 | **9c** | | 92 | |
| 10 | **1j** | 2-$NO_2C_6H_4$ | CHO | THF | $CaCO_3$ | 40 | 5.5 | **9d** | | 87 | |
| 11 | **1k** | 4-$NO_2C_6H_4$ | CHO | THF | $CaCO_3$ | 40 | 1 | **9e** | | 91 | |
| 12 | **1b** | 4-$MeC_6H_4$ | Ph | EtOH (95% aq) | — | 70 | 14 | **10a** | | | 60[d] |
| 13 | **1e** | 4-$MeOC_6H_4$ | Ph | EtOH (95% aq) | — | 70 | 40 min | **10b** | | | 54[e] |
| 14 | **1k** | 4-$NO_2C_6H_4$ | Ph | EtOH (95% aq) | — | 70 | 45 min | **10c** | | | 83[f] |

[a] Yield of pure product after column chromatography.
[b] The reaction was incomplete (a test of azo coupling with 2-naphthol was still positive).
[c] tr=traces.
[d] 1-(4-Tolyl)styrene was produced in 7% yield (see Section 4).
[e] 1-(4-Methoxyphenyl)styrene was produced in 16% yield (see Section 4).
[f] 1-(4-Nitrophenyl)styrene was produced in 6% yield (see Section 4).

**Table 3**. 1-Arylcyclopentenes **12a–i**

| Entry no. | Starting compound **1** | Ar in **1**, **12** | Product **12** | Solvent | Reaction time at rt (min) | Yield (%)[a] of **12** (ratio 1-Ar:3-Ar)[b] | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | From **1** | From $BF_4^-$ | From lit. |
| 1 | **1a** | 2-$MeC_6H_4$ | **12a** | EtOH (95% aq) | 15 | 70 (97.4:2.6) | | 24 (0:100)[c,4c] |
| 2 | **1b** | 4-$MeC_6H_4$ | **12b** | EtOH (95% aq) | 10 | 84 (100:0) | 73 (94:6) | 41 (70:30)[c,4a], 30 (54:46)[d,4a], 53 (50:50)[e,4a], 71 (50:50)[c,4c], 46 (10:90)[f,4c], 89 (5:95)[g,5b] |
| 3 | **1c** | 2-$MeOC_6H_4$ | **12c** | EtOH (95% aq) | 10 | 81 (99:1) | | |
| 4 | **1d** | 3-$MeOC_6H_4$ | **12d** | EtOH (95% aq) | 20 | 77 (98.2:1.8) | | |
| 5 | **1e** | 4-$MeOC_6H_4$ | **12e** | EtOH (95% aq) | 15 | 89 (98.7:1.3) | | 30 (46:54)[c,4c], 31 (2:98)[f,4c] |
| 6 | **1f** | 4-$ClC_6H_4$ | **12f** | EtOH (95% aq) | 10 | 83 (97.5:2.5) | 73 (86:14) | 35 (100:0)[f,4c], 75 (20:80)[h,5j], 72 (20:80)[g,5i], 10 (10:90)[d,4a], 49 (0:100)[c,4c] |
| 7 | | | | MeCN | 10 | 77 (31:63:6)[i] | | |
| 8 | | | | $CH_2Cl_2$ | 24 h[j] | [k] | | |
| 9 | **1h** | 4-$BrC_6H_4$ | **12g** | EtOH (95% aq) | 15 | 90 (100:0) | | 41 (99:1)[f,4c] |
| 10 | **1j** | 2-$NO_2C_6H_4$ | **12h** | EtOH (95% aq) | 30 | 90 (100:0) | | 5 (0:100)[c,4c] |
| 11 | **1k** | 4-$NO_2C_6H_4$ | **12i** | EtOH (95% aq) | 5 | 90 (100:0) | 84 (79:21) | 32 (5:95)[g,5b], 11 (0:100)[c,4a], 11 (0:100)[d,4c] |
| 12 | | | | EtOH (absolute) | 15 | 73 (100:0) | | |
| 13 | | | | THF | 2.5 h[j] | 89 (100:0) | | |

[a] Yield of pure product after column chromatography.
[b] Determined by GC analysis.
[c] From the tetrafluoroborate in MeCN, in the presence of $Pd(dba)_2$/MeCOONa.
[d] From the chloride in aqueous MeCN, in the presence of $LiPdCl_3$/HCOONa.
[e] As in note c, in the presence of $Pd(dba)_2$/HCOONa.
[f] As in note c, in $CH_2Cl_2$.
[g] From the trifluoroacetate in EtOH, in the presence of $Pd(dba)_2$.
[h] As in note g, starting from the tetrafluoroborate.
[i] GC ratio of regioisomers 1-Ar:3-Ar:4-Ar.
[j] At 40 °C.
[k] The reaction failed.

and independently of their position, whether *ortho*, *meta* or *para*, on the aromatic ring. In entries 6, 9 and 28, procedure A was carried out at rt: the reaction times were obviously longer, varying from 90 min to 17 h, but the arylation product yields were clearly much better. Procedure B failed in the case of 3-bromobenzenediazonium *o*-benzenedisulfonimide (**1g**; entry 16), and only in a few cases (entries 4, 7, 26 and 33), did it furnish higher yields with respect to those obtained with procedure A.

All the ethyl cinnamates **7a–o** were obtained exclusively with an (*E*)-configuration, in good to optimal yields. With procedure A the yields varied between 70 and 97% (the average yield on 15 considered examples was 84%), with procedure B the yields varied between 42 and 100% (the average yield on 14 considered examples was 81%). It is to be also noted that entries 15–20, involving salts containing a bromide or iodide substituent on the aromatic ring (**1g**,**h**,**i**), show high chemoselectivity in that the only diazonium group reacted, as demonstrated by the reaction products that were exclusively the ethyl 3- or 4-bromo(or iodo)cinnamates (**7g**,**h**,**i**); this is similar to that reported in the literature for the halide substituted tetrafluoroborates.[5e,f,j]

Still with regard to yields of ethyl cinnamates **7**, Table 1 shows that our yields, obtained using the dry arenediazonium *o*-benzenedisulfonimides **1**, are comparable with those reported in the literature starting from the corresponding arenediazonium tetrafluoroborates or trifluoroacetates, the sole exception being the 2-carboxybenzenediazonium *o*-benzenedisulfonimide (**1l**), which gave much higher yields (entries 25, 26). Furthermore, it is quite significant to note that all the nitrosubstituted benzenediazonium *o*-benzenedisulfonimides **1j**,**k**,**n** gave arylation products in excellent yields (81–100%, entries 21–24 and 30, 31). This stands in contrast with the difficulties reported in the literature starting from the corresponding nitrosubstituted tetrafluoroborates[4b,c,5a,j] or trifluoroacetates,[5b] in the presence of various palladium catalysts. To clarify this discordance we performed the Heck-arylation of ethyl acrylate (**2**) with 2-nitrobenzenediazonium and 4-nitrobenzenediazonium tetrafluoroborates under the same conditions as in entries 21 and, respectively, 23 and 24. These salts behaved in exactly the same way as the corresponding *o*-benzenedisulfonimides **1j** and **1k**, and ethyl cinnamates **7j** and **7k** were obtained in comparable yields (see Sections 4.8.1, 4.8.2 and 4.8.3). Note also that excellent yields were recently obtained on reacting 4-nitrobenzenediazonium tetrafluoroborate with acrylic esters using a new Pd(0) catalyst, that is, (*E*,*E*,*E*)-1-ferrocenylsulfonyl-6,11-bis[(4-methylphenyl)sulfonyl]-1,6,11-triazaciclopentadeca-3,8,13-trienepalladium(0), that is, however, of both elaborate and very expensive synthesis.[6b]

To substantiate the validity of the dry arenediazonium *o*-benzenedisulfonimides **1** as electrophiles in Heck-type arylations, reactions with other substrates containing C–C multiple bonds, that is, acrylic acid (**3**), acroleyne (**4**), styrene (**5**) and cyclopentene (**11**), were carried out.

### 2.2. Heck-type arylation of acrylic acid (3) and acroleyne (4) with dry arenediazonium *o*-benzenedisulfonimides 1 to give (*E*)-cinnamic acids 8a–d and (*E*)-cinnamic aldehydes 9a–e

There are few examples[5h,6g] of Heck-type coupling reactions of arenediazonium salts with acrylic acid (**3**). However, a recent patent[6e] reports the Heck arylation of **3** with various arenediazonium salts prepared in situ from the corresponding anilines; the aim of the patent was to prepare polyhalogenated cinnamic acids useful for the preparation of indanones, which are precursors of agro- and pharmaceutical chemicals, and of substances endowed with liquid-crystalline properties.

Some representative dry arenediazonium *o*-benzenedisulfonimides **1** were reacted with acrylic acid (**3**) in a molar ratio of 1:1.5 in anhydrous THF at 40–60 °C, in the presence of anhydrous $CaCO_3$ as the base (in equimolar amount with respect to the acid) and $Pd(OAc)_2$ (1 mol% with respect to the salt **1**) as pre-catalyst. The results are shown in Table 2 (entries 1–5). The reaction times were varied from 3.5 to 48 h. The use of anhydrous MeCN as the solvent, and of MeCOONa as the base, shortened the reaction times (compare entries 3 and 2). The cinnamic acids **8** were obtained exclusively in the (*E*)-configuration, the yields varying from 55 to 96% (the average yield on the five considered examples was 74%). The reaction of entry 2, carried out in the same reaction conditions but substituting THF with EtOH gave (*E*)-ethyl 4-methoxycinnamate (**7e**) via tandem Heck-esterification reactions (see Section 4.4.5), as reported in the literature starting from the tetrafluoroborates.[5h,6g]

Likewise, some representative (*E*)-cinnamic aldehydes **9** were prepared by reacting the dry salts **1** with acroleyne (**4**). The conditions and results are shown in Table 2 (entries 6–11). As can be seen, the reaction of 4-methoxybenzenediazonium *o*-benzenedisulfonimide (**1e**) failed in THF/$CaCO_3$ at 40 °C (entry 7), whereas there were good results in MeCN/MeCOONa at rt (entry 8). The average yield of the five considered examples was 90%.

With regard to the Heck arylation of acroleyne with diazonium salts, the only example reported in the literature is the one related to the synthesis of (*E*)-4-methoxycinnamic aldehyde (**9b**) that was obtained in 71% yield starting from 4-methoxybenzenediazonium tetrafluoroborate.[5a]

### 2.3. Heck-type arylation of styrene (5) with dry arenediazonium *o*-benzenedisulfonimides 1 to give (*E*)-stilbenes 10a–c

Amongst the most interesting substrates for Heck-type coupling reactions are styrene and the stilbenes, particularly in view of their use in the preparation of conjugated aromatic oligomers and polymers.[9] As stated for the acrylic esters, also many stilbenes have been prepared, always in good[4a,c,d,5b,e] to excellent[6b] yields, possessing an (*E*)-configuration, by the reaction of styrene with arenediazonium salts, mainly the tetrafluoroborates, as such[4c,5e,6b] or generated in situ by diazotization of anilines,[4a,d] but also trifluoroacetates,[5b] in the presence of various palladium catalysts/pre-catalysts.

In the present work, various salts **1** were reacted with styrene (**5**), in a molar ratio of 1:1.2, in the presence of $Pd(OAc)_2$, 1 mol% with respect to salt **1**, as pre-catalyst. The reactions, which were carried out in 95% aqueous EtOH at 70 °C, reached completion in times of between 40 min and 14 h, and were not completely regioselective. In fact, along with the stilbenes **10**, varying amounts of 1-arylstyrenes (6–16% yields) were also formed. However, column chromatography on the crude reaction mixtures, avoiding sunlight to prevent known photoisomerization,[9a] provided stilbenes **10a–c**, with an (*E*)-configuration exclusively, in good yields (from 54 to 83%). The results are shown in Table 2 (entries 12–14).

### 2.4. Heck-type arylation of cyclopentene (11) with dry arenediazonium *o*-benzenedisulfonimides 1 to give 1-arylcyclopentenes 12a–i

The palladium-catalyzed Heck-type arylations of cyclopentene with both aryl halides and arenediazonium salts usually result in a mixture of all the possible regioisomers, their formation being explained in terms of the isomerization of the initial arylation product that is the 3-arylcyclopentene.[4c]

To the best of our knowledge, the reactions carried out on the cyclopentene (**11**) with diazonium salts like the tetrafluoroborates,[4c,5j] chlorides[4a] or trifluoroacetates, as such[5b] or generated in situ,[5i] gave, in most cases, mixtures of two isomers, the 1-arylcyclopentenes and the 3-arylcyclopentenes, generally with a prevalence for the 3-aryl isomer, in low to modest yields. This is independent of the catalyst and the solvent used and of the type of substituent present on the diazonium salt (see Table 3). Only one report[4c] details the exclusive formation, or definite prevalence, of 1-aryl isomers, precisely 1-(4-chlorophenyl)cyclopentene (35% yield), and 1-(4-bromophenyl)cyclopentene (41% yield), 1-(3-tolyl)cyclopentene (27% yield) and 1-(3-chlorophenyl)cyclopentene (75% yield), contaminated, respectively, by 1, 6 and 10% of the 3-aryl isomers. These reactions were carried out on the tetrafluoroborates in $CH_2Cl_2$, at rt, in the presence of $Pd(dba)_2$/MeCOONa. For the reactions of salts **1** with **11**, we chose the conditions previously[5b,i,j] reported for the Heck reaction of cyclopentene, that is, at rt in EtOH and in the presence of $Pd(OAc)_2$. However, in the literature only five salts have been tested: 4-chlorobenzenediazonium tetrafluoroborate[5j] or trifluoroacetate[5i] and 4-(Boc-amino)benzenediazonium, 4-toluenediazonium and 4-nitrobenzenediazonium trifluoroacetates.[5b] The first two salts gave mixtures of the two isomers 1-aryl and 3-aryl, in a ratio of 1:5 (as shown by GC) in favor of the second, in yields of 75 and 72%, respectively. The other three salts gave 3-arylcyclopentenes contaminated by 5% (by $^1$H NMR spectroscopy) of 1-aryl isomers, in yields of 77, 89 and 32%, respectively.

A variety of salts **1** were reacted with cyclopentene (**11**) in a molar ratio of 1:1.2, in 95% aqueous EtOH at rt in the presence of $Pd(OAc)_2$ (1 mol% with respect to salt **1**). The reactions proceeded to completion in short times (5–30 min) and gave the 1-arylcyclopentenes (**12**) as sole products (Table 3, entries 2, 9–13) or, in some cases, accompanied by small amounts of 3-arylcyclopentenes (GC analysis showed $<2.6\%$; entries 1, 3–6). The high selectivity of these

reactions were shown to be independent of the electron and steric effects of the substituents. Yields of the products **12** were excellent, varying between 70 and 90%; the average yield of the nine examples was 84%. To evaluate the effect of the solvent, 4-nitrobenzenediazonium *o*-benzenedisulfonimide (**1k**) was reacted with **11** also in absolute EtOH at rt, and in anhydrous THF at 40 °C (entries 12, 13). These reactions gave the sole isomer 1-(4-nitrophenyl)cyclopentene (**12i**), in yields just a little lower than or comparable to that of entry 11, carried out in 95% aqueous EtOH. With the same goal in mind, 4-chlorobenzenediazonium *o*-benzenedisulfonimide (**1f**) was reacted with **11** also in MeCN at rt and in $CH_2Cl_2$ at about 40 °C (entries 7, 8). The first reaction showed no selectivity in that it gave three isomers, that is, 1-aryl, 3-aryl and 4-aryl, in a ratio of 31:63:6 (as shown by GC) in favor of the 3-aryl. Instead the second reaction failed, probably because of the low solubility of the salt in the latter solvent. Also of particular note are the excellent yields (90%) obtained in entries 10 and 11 by reacting, respectively, 2-nitrobenzenediazonium and 4-nitrobenzenediazonium *o*-benzenedisulfonimides (**1j** and **1k**) with **11**. The literature, instead, reports that the Heck arylations of cyclopentene with nitrosubstituted arenediazonium salts always give low yields[4a,c,5b] (from 5 to 32%), the main reaction product always being nitrobenzene. To compare the reactivity of our salts **1** with that of the corresponding tetrafluoroborates, we always reacted some representative tetrafluoroborates, namelyl 4-toluenediazonium, 4-chlorobenzenediazonium and 4-nitrobenzenediazonium tetrafluoroborates, with **11**, in the conditions cited above for entries 2, 6, 11. In our hands, all three salts gave 1-aryl and 3-aryl isomer mixtures, with the first clearly prevailing; this is in disagreement with that reported in the literature. The results, shown in Table 3, highlight that, under the same reaction conditions, the selectivity of the tetrafluoroborates is lower than that of salts **1**.

## 3. Conclusion

In conclusion, this research has demonstrated the validity of a recent family of stable diazonium salts in the dry state, the arenediazonium *o*-benzenedisulfonimides **1**, as new and efficient reagents in Heck-type arylation reactions of several common substrates containing C–C multiple bonds, namely ethyl acrylate (**2**), acrylic acid (**3**), acroleyne (**4**), styrene (**5**) and cyclopentene (**11**). The proposed procedures are general in that they give positive results in the presence of both electron withdrawing and electron donating substituents, not suffering steric effects and affording arylation products, that is, ethyl cinnamates **7**, cinnamic acids **8**, cinnamic aldehydes **9**, stilbenes **10**, possessing an (*E*)-configuration, and 1-arylcyclopentenes **12**, in good to excellent yields. It is to be noted that in most of the reported reactions the salts **1** are in parallel[10] with the class of tetrafluoroborates, which are well-known from a long time, or the most recent trifluoroacetates. However, the use of the arenediazonium *o*-benzenedisulfonimides **1** has several advantages over the use of the other salts: (i) easy preparation and high stability, thus allowing them to be kept ready for use for long periods; (ii) possibility of recovery, at the end of the reactions, of *o*-benzenedisulfonimide (**6**), that unlike tetrafluoroboric or trifluoroacetic acids, is a non-risk acid that can be reused to prepare other salts **1**, with ecological and economic advantages. Once again it must be underlined that, with regard to the reactions of salts **1** with cyclopentene (**11**), our direct comparison of the two classes of salts, that is, salts **1** and the corresponding tetrafluoroborates, in the same reaction conditions, revealed still a parallel behavior, but there was a very clear synthetic superiority of the salts **1**, that led to the 1-arylcyclopentenes (**12**) with greater purity.

## 4. Experimental

### 4.1. General

All of the reactions were performed in oven-dried glassware when anhydrous solvent was used. No particular device was, however, adopted to exclude moisture or oxygen. Column chromatography and TLC were performed on Merck silica gel 60 (70–230 mesh ASTM) and GF 254, respectively. Petroleum ether refers to the fraction boiling in the range 40–60 °C and is abbreviated as PE. Room temperature (20–25 °C) is abbreviated as rt. Details for the reactions and yields of the pure (GC, GC–MS, TLC, $^1$H NMR) isolated (*E*)-ethyl cinnamates **7a–o**, (*E*)-cinnamic acids **8a–d**, (*E*)-cinnamic aldehydes **9a–e**, (*E*)-stilbenes **10a–c**, and 1-arylcyclopentenes **12a–i** are listed in Tables 1–3. Structures and purity of all the products were confirmed by comparison of their physical (mp or bp) and spectral data (MS, $^1$H NMR) with those reported in the literature or with those of the corresponding commercially available samples of analytical purity. All of the amines and olefins, solvents and all of the reference compounds were purchased from the Aldrich Chemical Co. Dowex 50X8 ion-exchange resin was purchased from Fluka.

### 4.2. Dry arenediazonium *o*-benzenedisulfonimides 1

Dry arenediazonium *o*-benzenedisulfonimides **1a–h**,**j**,**k**,[1a,b] **1i**,[11a] **1m**[11b] and **1n**[11c] were prepared as described previously. According to the same general procedure, the new salts 2-carboxybenzenediazonium *o*-benzenedisulfonimide (**1l**) and 2-methoxycarbonyl-3-tiophenediazonium *o*-benzenedisulfonimide (**1o**) were also prepared. The crude salts were pure (by $^1$H NMR spectroscopy) and could be used in the subsequent Heck-type arylation, without further crystallization.

**4.2.1. Dry 2-carboxybenzenediazonium *o*-benzenedisulfonimide (1l).** Diazotization of 2-aminobenzoic acid (1.37 g, 10 mmol) was carried out with *i*-pentyl nitrite (1.29 g, 11 mmol) in HCOOH (30 ml), in the presence of *o*-benzenedisulfonimide (**6**; 2.63 g, 12 mmol), at 0–5 °C. The virtually pure ($^1$H NMR, dp=decomposition point) title compound was obtained in >99% yield (3.67 g). For analytical purposes, a sample was purified by dissolution in HCOOH and precipitation with anhydrous $Et_2O$ after cooling: dp 135 °C; MS *m*/*z* 367 ($M^+$); $^1$H NMR (200 MHz, $CD_3CN/CD_3COCD_3$): $\delta$ 7.64–7.78 (m, 4H), 8.14 (t, $J$=8.0 Hz, 1H), 8.34 (t, $J$=8.0 Hz, 1H), 8.44 (ddd, $J$=7.7, 1.5 Hz, 1H), 8.69 ppm (ddd, $J$=8.3, 1.2 Hz, 1H); $^{13}$C NMR ($D_2O$/DCl): $\delta$ 115.5 (s), 122.4 (d, 2C), 132.8 (s), 134.7 (d), 135.3 (d, 2C), 136.6 (d, 2C), 141.2 (s, 2C), 142.3 (d), 163.6 (s). Anal. Calcd for $C_{13}H_9N_3O_6S_2$ (367.35): C,

42.51; H, 2.47; N, 11.44; S, 17.45. Found: C, 42.44; H, 2.51; N, 11.33; S, 17.40.

**4.2.2. Dry 2-methoxycarbonyl-3-tiophenediazonium *o*-benzenedisulfonimide (1o).** Yield: 97% (3.76 g); dp 161.6–162.8 °C; MS *m/z* 359 ($M^+ - N_2$); $^1$H NMR (200 MHz, $CD_3CN/CD_3COCD_3$): $\delta$ 4.04 (s, 3H), 7.61–7.72 (m, 4H), 8.16 (d, $J=5.6$ Hz, 1H), 8.19 (d, $J=5.6$ Hz, 1H); $^{13}$C NMR ($D_2O/DCl/CD_3COCD_3$): $\delta$ 51.4 (q), 103.6 (s), 118.0 (d, 2C), 125.4 (d), 131.0 (d, 2C), 132.5 (d), 135.6 (s, 2C), 145.4 (s), 154.3 (s). Anal. Calcd for $C_{12}H_9N_3O_6S_3$ (387.40): C, 37.20; H, 2.34; N, 10.85; S, 24.83. Found:C, 37.15; H, 2.28; N, 10.77; S, 24.77.

CAUTION! In our laboratory was no case of sudden decomposition during the preparation, purification, and handling of salts **1**. Nevertheless it must be born in mind that all diazonium salts in the dry state are potentially explosive. Therefore, they must be carefully stored and handled.

### 4.3. Heck-type reactions of dry arenediazonium *o*-benzenedisulfonimides 1 with ethyl acrilate (2); representative procedures

**4.3.1. Procedure A. (*E*)-Ethyl 4-nitrocinnamate (7k).** In entry 23 of Table 1, 4-nitrobenzenediazonium *o*-benzenedisulfonimide (**1k**; 0.55 g, 1.5 mmol) was added in one portion with stirring to a solution of ethyl acrilate (**2**; 0.18 g, 1.8 mmol) and $Pd(OAc)_2$ (1 mol%; 0.004 g, 0.015 mmol) in absolute EtOH (15 ml) and the reaction mixture was placed in an oil bath at 70 °C. The salt dissolved at once, and the resultant solution became temporarily deep red and then turned quickly to brown; simultaneously, a plentiful evolution of nitrogen took place. A test of azo coupling with 2-naphthol was negative 5 min after the addition of the salt. This confirmed a sudden reaction of **1k**. TLC ($PE/Et_2O$, 7:3), GC, and GC–MS analyses of the reaction mixture showed the presence of the title compound as major product, beside the unreacted ethyl acrilate. The reaction 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 extracted with $Et_2O$ ($2\times20$ ml). The combined organic extracts were washed with $H_2O$ (20 ml), dried over $Na_2SO_4$, and evaporated under reduced pressure. The crude residue was chromatographed on a short column ($PE/Et_2O$, 7:3) to provide the pure (GC, GC–MS, TLC, $^1$H NMR) title compound in 97% yield (0.32 g); mp 138.5–139 °C, from EtOH; MS *m/z* 221 ($M^+$); physical and $^1$H NMR data identical to those of a commercially available sample of analytical purity.

The aqueous layer and aqueous washings were collected and evaporated under reduced pressure. The residue was passed through a column of Dowex 50X8 ion-exchange resin (1.6 g for 1 g of product), eluting with $H_2O$ (about 35 ml). After removal of $H_2O$ under reduced pressure, virtually pure ($^1$H NMR) *o*-benzenedisulfonimide (**6**) was recovered in 85% yield (0.28 g); mp 192–194 °C, from toluene (lit.[1a] mp 192–194 °C).

**4.3.2. Procedure B. (*E*)-Ethyl 4-nitrocinnamate (7k).** The procedure B differs from the former only for the solvent (95% aqueous EtOH) and for the reaction temperature (rt). The title compound obtained by chromatography of the crude residue, had physical and $^1$H NMR spectroscopic data identical to those of the above product.

Details for the reactions and yields of products **7a–o** are listed in Table 1.

**4.3.3. (*E*)-Ethyl 2-methylcinnamate (7a).** Chromatographic solvent: $PE/Et_2O$, 9:1; colorless oil: bp 130 °C/1.5 mmHg (lit.[12] bp 148 °C/1.2 mmHg); MS *m/z* 190 ($M^+$); $^1$H NMR spectroscopic data identical to that reported.[6b]

**4.3.4. (*E*)-Ethyl 4-methylcinnamate (7b).** Chromatographic solvent: $PE/Et_2O$, 9:1; colorless oil: bp 147 °C/2 mmHg; MS *m/z* 190 ($M^+$); physical and $^1$H NMR spectroscopic data identical to those of a commercially available sample of analytical purity (Aldrich).

**4.3.5. (*E*)-Ethyl 2-methoxycinnamate (7c).** Chromatographic solvent: $PE/Et_2O$, 4:1; mp 33–34 °C, from PE (lit.[13] mp 35 °C); MS *m/z* 206 ($M^+$); $^1$H NMR spectroscopic data identical to those reported.[14]

**4.3.6. (*E*)-Ethyl 3-methoxycinnamate (7d).** Chromatographic solvent: $PE/Et_2O$, 4:1; colorless oil: bp 145 °C/1.5 mmHg (lit.[12] bp 185–186 °C/15 mmHg); MS *m/z* 206 ($M^+$); $^1$H NMR spectroscopic identical to that reported.[14]

**4.3.7. (*E*)-Ethyl 4-methoxycinnamate (7e).** Chromatographic solvent: $PE/Et_2O$, 7:3; mp 49.5–51 °C, from PE (lit.[12] mp 49–50 °C); MS *m/z* 206 ($M^+$); $^1$H NMR spectroscopic data identical to that reported.[15]

**4.3.8. (*E*)-Ethyl 4-chlorocinnamate (7f).** Chromatographic solvent: $PE/Et_2O$, 9:1; colorless oil: bp 136–137 °C/0.8 mmHg (lit.[13] bp 160 °C/11 mmHg); MS *m/z* 210 ($M^+$); $^1$H NMR spectroscopic data identical to that reported.[15]

**4.3.9. (*E*)-Ethyl 3-bromocinnamate (7g).** Chromatographic solvent: $PE/Et_2O$, 9:1; mp 37 °C, from EtOH (lit.[12,16] oil); MS *m/z* 254 ($M^+$); $^1$H NMR spectroscopic data identical to that reported.[16]

**4.3.10. (*E*)-Ethyl 4-bromocinnamate (7h).** Chromatographic solvent: $PE/Et_2O$, 9:1; colorless oil: bp 158 °C/1.5 mmHg; MS *m/z* 254 ($M^+$); physical and $^1$H NMR spectroscopic data identical to those of a commercially available sample of analytical purity.

**4.3.11. (*E*)-Ethyl 4-iodocinnamate (7i).** Chromatographic solvent: $PE/Et_2O$, 9:1; mp 35–36 °C, from PE (lit.[17] mp 38–39 °C); MS *m/z* 302 ($M^+$); $^1$H NMR spectroscopic data identical to that reported.[17]

**4.3.12. (*E*)-Ethyl 2-nitrocinnamate (7j).** Chromatographic solvent: $PE/Et_2O$, 7:3; mp 42–43 °C, from EtOH (lit.[12] mp 44 °C); MS *m/z* 221 ($M^+$); $^1$H NMR spectroscopic data identical to that reported.[15]

**4.3.13. (*E*)-Ethyl 2-carboxycinnamate (7l).** Chromatographic solvent: $CHCl_3$/MeOH, 9.5:0.5; mp 85.5–86.5 °C, from $CHCl_3$/PE (lit.[12] mp 95 °C); MS *m/z* 220 ($M^+$); $^1$H

NMR ($CDCl_3$, 200 Hz): $\delta$ 1.41 (t, $J$=7.1 Hz, 3H), 4.36 (q, $J$=7.1 Hz, 2H), 6.39 (d, $J$=15.9 Hz, 1H), 8.63 (d, $J$=15.9 Hz, 1H), 7.61–7.70 (m, 3H), 8.19 (m, 1H).

**4.3.14. (*E*)-Ethyl 4-cianocinnamate (7m).** Chromatographic solvent: PE/$Et_2O$, 3:2; mp 69–69.3 °C, from EtOH; MS *m/z* 201 ($M^+$); physical and $^1H$ NMR spectroscopic data identical to those of a commercially available sample of analytical purity.

**4.3.15. (*E*)-Ethyl 2,4-dinitrocinnamate (7n).** Chromatographic solvent: PE/$Et_2O$, 3:2; mp 94.6–95.4 °C, from EtOH (lit.[12] mp 94 °C); MS *m/z* 266 ($M^+$); $^1H$ NMR spectroscopic data identical to that reported.[18]

**4.3.16. (*E*)-Ethyl 3-(2-methoxycarbonyl-3-thienyl)pronenoate (7o).** Chromatographic solvent: PE/$Et_2O$, 7:3; mp 65.5–66 °C, from PE; MS *m/z* 240 ($M^+$); $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 1.34 (t, $J$=7.1 Hz, 3H), 3.92 (s, 3H), 4.28 (q, $J$=7.1 Hz, 2H), 6.38 (d, $J$=15.8 Hz, 1H), 8.51 (d, $J$=15.8 Hz, 1H), 7.35 (d, $J$=5.3 Hz, 1H), 7.47 (d, $J$=5.3 Hz, 1H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 14.5 (q), 52.5 (q), 60.9 (t), 122.3 (d), 126.8 (d), 131.0 (d), 131.3 (s), 136.7 (d), 142.1 (s), 162.5 (s), 166.9 (s). Anal. Calcd for $C_{11}H_{12}O_4S$ (240.27): C, 54.99; H, 5.03; S, 13.34. Found C, 55.02; H, 5.06; S, 13.40.

### 4.4. Heck-type reactions of dry arenediazonium *o*-benzenedisulfonimides 1 with acrilic acid (3); representative procedures

**4.4.1. (*E*)-4-Methylcinnamic acid (8a).** In entry 1 of Table 2, the reaction mixture constituted of 4-toluenediazonium *o*-benzenedisulfonimide (**1b**; 0.51 g, 1.5 mmol), acrilic acid (**3**; 0.16 g, 2.25 mmol), anhydrous $CaCO_3$ (0.22 g, 2.25 mmol), and $Pd(OAc)_2$ (1 mol%; 0.004 g, 0.015 mmol) in anhydrous THF (15 ml) and maintained under stirring, was placed in an oil bath at 60 °C. The reaction reached completion after 12 h (absence of azo coupling with 2-naphthol). The reaction mixture was evaporated under reduced pressure and then dissolved into a 5% aqueous NaOH solution (5–10 ml). The aqueous layer was extracted with $Et_2O$ (3×20 ml) and then acidified with dil HCl until complete precipitation of **8a**, which was extracted with $Et_2O$ (3×20 ml). The combined organic extracts were washed with $H_2O$ (20 ml), dried over $Na_2SO_4$, and evaporated under reduced pressure. The title compound was obtained virtually pure in 88% yield (0.21 g); mp 195.0–196.5 °C, from MeCOMe; MS *m/z* 162 ($M^+$); physical and $^1H$ NMR data identical to those of a commercially available sample of analytical purity. Working as described above, pure *o*-benzenedisulfonimide (**6**) was recovered in 80% yield (0.26 g).

**4.4.2. (*E*)-4-Methoxycinnamic acid (8b).** In entry 3 of Table 2, the reaction mixture constituted of 4-methoxybenzenediazonium *o*-benzenedisulfonimide (**1e**; 0.53 g, 1.5 mmol), acrilic acid (**3**; 0.16 g, 2.25 mmol), anhydrous MeCOONa (0.25 g, 3.0 mmol), and $Pd(OAc)_2$ (1 mol%; 0.004 g, 0.015 mmol) in anhydrous MeCN (10 ml) and maintained under stirring, was placed in an oil bath at 60 °C. The reaction reached completion after 6 h (absence of azo coupling with 2-naphthol). The above work-up provided the virtually pure title compound in 67% yield (0.18 g); mp 169.0–170.5 °C, from aqueous EtOH; MS *m/z* 178 ($M^+$); physical and $^1H$ NMR data identical to those of a commercially available sample of analytical purity. Pure *o*-benzenedisulfonimide (**6**) was recovered in 80% yield (0.26 g).

Details for the reactions and yields of products **8a–d** are listed in Table 2 (entries 1–5).

**4.4.3. (*E*)-4-Chlorocinnamic acid (8c).** Prepared according to the procedure described above for **8a**, starting from **1f**. Mp 249–250.3 °C, from EtOH; MS *m/z* 182 ($M^+$); physical and $^1H$ NMR data identical to those of a commercially available sample of analytical purity (Aldrich).

**4.4.4. (*E*)-4-Nitrocinnamic acid (8d).** Prepared according to the procedure described above for **8a**, starting from **1k**. Mp 291.5–292.6 °C, from EtOH (lit.[19] mp 286–287 °C); MS *m/z* 193 ($M^+$); $^1H$ NMR identical to that reported.[19]

**4.4.5. (*E*)-Ethyl 4-methoxycinnamate (7e).** According to the procedure A described above for the preparation of (*E*)-ethyl 4-nitrocinnamate (**7k**), a reaction mixture constituted of 4-methoxybenzenediazonium *o*-benzenedisulfonimide (**1d**; 0.53 g, 1.5 mmol), acrilic acid (**3**; 0.13 g, 1.80 mmol) and $Pd(OAc)_2$ (1 mol%; 0.004 g, 0.015 mmol) in absolute EtOH (15 ml) and maintained under stirring, was placed in an oil bath at 70 °C. The reaction was complete after 30 min (absence of azo coupling with 2-naphthol). TLC ($CHCl_3$), GC, and GC–MS analyses of the reaction mixture showed the presence of the title compound as major product. The crude residue, obtained after the usual work up, was chromatographed on a short column, eluting with $CHCl_3$. Compound **7e** was obtained pure in 52% yield (0.16 g); mp 49.5–51 °C, from PE; MS *m/z* 206 ($M^+$); physical and $^1H$ NMR data identical to those of the sample reported in Section 4.3.7.

### 4.5. Heck-type reactions of dry arenediazonium *o*-benzenedisulfonimides 1 with acroleyne (4); representative procedures

**4.5.1. (*E*)-4-Methylcinnamic aldehyde (9a).** In entry 6 of Table 2, the reaction mixture constituted of 4-toluenediazonium *o*-benzenedisulfonimide (**1b**; 0.51 g, 1.5 mmol), acroleyne (**4**; 0.13 g, 2.25 mmol), anhydrous $CaCO_3$ (0.22 g, 2.25 mmol) and $Pd(OAc)_2$ (1 mol%; 0.004 g, 0.015 mmol) in anhydrous THF (15 ml) and maintained under stirring, was placed in an oil bath at 40 °C. The reaction reached completion after 4.5 h (absence of azo coupling with 2-naphthol). TLC (PE), GC, and GC–MS analyses of the reaction mixture showed the presence of **9a** as major product, beside the unreacted starting acroleyne. A work-up identical to that decribed above for *E*-ethyl 4-nitrocinnamate (**7k**), afforded a crude residue that was chromatographed on a short column (PE/$Et_2O$, 4:1). The title compound **9a** was obtained pure in 95% yield (0.21 g); mp 43.4–44.5 °C, from aqueous EtOH; MS *m/z* 146 ($M^+$); physical and $^1H$ NMR data identical to those of a commercially available sample of analytical purity. Pure *o*-benzenedisulfonimide (**6**) was recovered in 80% yield (0.26 g).

**4.5.2. (*E*)-4-Methoxycinnamic aldehyde (9b).** In entry 8 of Table 2, the reaction mixture constituted of 4-methoxybenzenediazonium *o*-benzenedisulfonimide (**1e**; 0.53 g, 1.5 mmol), acroleyne (**4**; 0.13 g, 2.25 mmol), anhydrous MeCOONa (0.13 g, 1.5 mmol) and $Pd(OAc)_2$ (1 mol%; 0.004 g, 0.015 mmol) in anhydrous MeCN (10 ml) was stirred at rt for 3 h, until completion of the reaction (absence of azo coupling with 2-naphthol). The crude residue, obtained after the above work-up, was chromatographed through a short column (PE/$Et_2O$, 7:3) to provide the pure title compound **9b** in 83% yield (0.20 g); mp 58.5–59.8 °C, from PE; MS *m*/*z* 162 ($M^+$); physical and $^1H$ NMR data identical to those of a commercially available sample of analytical purity. Pure *o*-benzenedisulfonimide (**6**) was recovered in 85% yield (0.28 g).

**4.5.3. (*E*)-4-Chlorocinnamic aldehyde (9c).** Prepared as described above for **9a**, starting from **1f**. Chromatographic solvent: PE/$Et_2O$, 4:1; mp 61–62 °C, from EtOH; MS *m*/*z* 166 ($M^+$); physical and $^1H$ NMR data identical to those of a commercially available sample of analytical purity (Aldrich).

**4.5.4. (*E*)-2-Nitrocinnamic aldehyde (9d).** Prepared as described above for **9a**, starting from **1j**. Chromatographic solvent: PE/$Et_2O$, 3:2; mp 126.8–127.1 °C, from EtOH; MS *m*/*z* 177 ($M^+$); physical and $^1H$ NMR data identical to those of a commercially available sample of analytical purity (Aldrich).

**4.5.5. (*E*)-4-Nitrocinnamic aldehyde (9e).** Prepared as described above for **9a**, starting from **1k**. Chromatographic solvent: PE/$Et_2O$, 3:2; mp 137–138.2 °C, from $CHCl_3$/PE; MS *m*/*z* 177 ($M^+$); physical and $^1H$ NMR data identical to those of a commercially available sample of analytical purity (Aldrich).

Details for the reactions and yields of products **9a–e** are listed in Table 2 (entries 6–11).

### 4.6. Heck-type reactions of dry arenediazonium *o*-benzenedisulfonimides 1 with styrene (5); representative procedure

**4.6.1. (*E*)-4-Nitrostilbene (10c).** In entry 14 of Table 2, the reaction mixture constituted of 4-nitrobenzenediazonium *o*-benzenedisulfonimide (**1k**; 0.55 g, 1.5 mmol), styrene (**5**; 0.19 g, 1.8 mmol) and $Pd(OAc)_2$ (1 mol%; 0.004 g, 0.015 mmol) in 95% aqueous EtOH (15 ml) and maintained under stirring, was placed in an oil bath at 70 °C. The reaction reached completion after 45 min (absence of azo coupling with 2-naphthol). GC–MS analysis of the crude residue, obtained after a work-up identical to that described above for (*E*)-ethyl 4-nitrocinnamate (**7k**), showed the presence of three products: nitrobenzene, MS *m*/*z* 123 ($M^+$), 1-(4-nitrophenyl)-1-phenylethylene, MS *m*/*z* 225 ($M^+$), and (*E*)-4-nitrostilbene, MS *m*/*z* 225 ($M^+$), as major product. These were isolated by chromatography on a short column (PE/$Et_2O$, 4:1), sheltered from the sunlight. The first eluted product was nitrobenzene (0.02 g, 10% yield). The second eluted product was 1-(4-nitrophenyl)-styrene (0.02 g, 6% yield); $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 5.50 (s, 1H), 5.53 (s, 1H), 7.20–7.40 (m, 5H), 7.50 (d, $J$=9.0 Hz, 2H), 8.20 (d, $J$=9.0 Hz, 2H). The third eluted product was the title compound **10c** (0.28 g, 83%); mp 157.2–157.8, from EtOH (lit.[12] mp 155 °C); $^1H$ NMR identical to that reported.[5b] Pure *o*-benzenedisulfonimide (**6**) was recovered in 85% yield (0.28 g).

Details for the reactions and yields of products **10a–c** are listed in Table 2 (entries 12–14).

**4.6.2. (*E*)-4-Methylstilbene (10a).** Chromatographic solvent: PE/$Et_2O$, 3:2; mp 118.5–119 °C, from EtOH; MS *m*/*z* 194 ($M^+$); physical and $^1H$ NMR data identical to those of a commercially available sample of analytical purity. The by product 1-(4-tolyl)styrene was isolated in 7% yield (0.02 g); MS: *m*/*z*=194 ($M^+$); $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 2.36 (s, 3H), 5.40 (d, $J$=1.6 Hz, 1H), 5.42 (d, $J$=1.6 Hz, 1H), 7.13 (d, $J$=8.3 Hz, 2H), 7.23 (d, $J$=8.30 Hz, 2H), 7.22–7.32 (m, 5H).

**4.6.3. (*E*)-4-Methoxystilbene (10b).** Chromatographic solvent: PE/$Et_2O$, 3:2; mp 136–136.5 °C, from EtOH (lit.[12] mp 137 °C); MS *m*/*z* 210 ($M^+$); $^1H$ NMR identical to that reported.[5b] The by product 1-(4-methoxyphenyl)-styrene was isolated in 16% yield (0.05 g); MS *m*/*z* 210 ($M^+$); $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 3.82 (s, 3H), 5.35 (d, $J$=1.7 Hz, 1H), 5.39 (d, $J$=1.7 Hz, 1H), 6.86 (d, $J$=8.7 Hz, 2H), 7.27 (d, $J$=8.7 Hz, 2H), 7.32–7.34 (m, 5H).

### 4.7. Heck-type reactions of dry arenediazonium *o*-benzenedisulfonimides 1 with cyclopentene (11); representative procedure

**4.7.1. 1-(4-Nitrophenyl)cyclopentene (12i).** In entry 11 of Table 3, the reaction mixture constituted of 4-nitrobenzenediazonium *o*-benzenedisulfonimide (**1k**; 0.55 g, 1.5 mmol), cyclopentene (**11**; 0.12 g, 1.8 mmol) and $Pd(OAc)_2$ (1 mol%; 0.004 g, 0.015 mmol) in 95% aqueous EtOH (15 ml) was stirred at rt until completion of the reaction (5 min; absence of azo coupling with 2-naphthol). TLC (PE/$Et_2O$, 9:1), GC, and GC–MS analyses of the crude residue, obtained after a work-up identical to that described above for (*E*)-ethyl 4-nitrocinnamate (**7k**), showed the presence of **12i**, as only arylation product. By chromatography on a short column (PE/$Et_2O$, 9:1), the title compound was obtained pure in 89.3% yield (0.25 g); mp 99.4–100 °C, from PE; MS *m*/*z* 189 ($M^+$); $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 1.99–2.14 (apparent quintet, 2H), 2.56–2.60 (m, 2H), 2.70–2.78 (m, 2H), 6.42 (m, 1H), 7.54 (d, $J$=8.3 Hz, 2H), 8.16 (d, $J$=8.3 Hz, 2H). Anal. Calcd for $C_{11}H_{11}NO_2$ (189.21): C, 69.83; H, 5.86; N, 7.40. Found C, 69.79; H, 5.82; N, 7.35. Compound **12i** has been mentioned in the literature,[4a,e,5b] but it was not isolated and its physical and spectral data were not reported. Pure *o*-benzenedisulfonimide (**6**) was recovered in 85% yield (0.28 g).

Details for the reactions and yields and purity of products **12a–i** are listed in Table 3.

**4.7.2. 1-(2-Tolyl)cyclopentene (12a).** Chromatographic solvent: PE. GC and GC–MS analyses showed a slight contamination (2.6%) of the regioisomer 3-(2-tolyl)cyclopentene (confirmed by $^1H$ NMR). Colorless oil: bp 144 °C/4 mmHg (lit.[20] bp 122–123 °C/25 mmHg); MS *m*/*z* 158

($M^+$); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ 1.96–2.07 (apparent quintet, 2H), 2.36 (s, 3H), 2.49–2.56 (m, 2H), 2.62–2.70 (m, 2H), 5.78 (m, 1H), 7.18–7.28 (m, 4H); identical to that reported.[21]

**4.7.3. 1-(4-Tolyl)cyclopentene (12b).** Chromatographic solvent: PE/$Et_2O$, 9.8:0.2; mp 51.8–52 °C, from EtOH (lit.[22] mp 50–51 °C); MS *m/z* 158 ($M^+$); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ 1.97–2.08 (apparent quintet, 2H), 2.33 (s, 3H), 2.44–2.60 (m, 2H), 2.60–2.76 (m, 2H), 6.13 (m, 1H), 7.12 (d, $J$=8.3 Hz, 2H), 7.33 (d, $J$=8.3 Hz, 2H); identical to that reported.[23]

**4.7.4. 1-(2-Methoxyphenyl)cyclopentene (12c).** Chromatographic solvent: PE/$Et_2O$, 9.8:0.2. GC and GC–MS analyses showed a slight contamination (1%) of the regioisomer 3-(2-methoxyphenyl)cyclopentene (confirmed by $^1$H NMR). Colorless oil: bp 122 °C/1.8 mmHg (lit.[24] bp 65 °C/0.05 mmHg); MS *m/z* 174 ($M^+$); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ 1.85–2.10 (apparent quintet, 2H), 2.48–2.68 (m, 2H), 2.68–2.85 (m, 2H), 3.87 (s, 3H), 6.44 (m, 1H), 6.82–7.00 (m, 2H), 7.12–7.34 (m, 2H); identical to that reported.[24]

**4.7.5. 1-(3-Methoxyphenyl)cyclopentene (12d).** Chromatographic solvent: PE/$Et_2O$, 9.8:0.2. GC and GC–MS analyses showed a slight contamination (1.8%) of the regioisomer 3-(3-methoxyphenyl)cyclopentene (confirmed by $^1$H NMR). Colorless oil: bp 143–144 °C/2 mmHg (lit.[25] bp 129–131 °C/13 mmHg); MS *m/z* 174 ($M^+$); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ 2.02–2.10 (apparent quintet, 2H), 2.50–2.65 (m, 2H), 2.65–2.85 (m, 2H), 3.86 (s, 3H), 6.22 (m, 1H), 6.75–6.85 (m, 1H), 6.98–7.12 (m, 2H), 7.20–732 (m, 1H); identical to that reported.[25]

**4.7.6. 1-(4-Methoxyphenyl)cyclopentene (12e).** Chromatographic solvent: PE/$Et_2O$, 9.8:0.2. GC and GC–MS analyses showed a slight contamination (1.3%) of the regioisomer 3-(4-methoxyphenyl)cyclopentene (confirmed by $^1$H NMR). After crystallization from EtOH, the title compound was obtained pure: mp 90.9–91.3 °C (lit.[22] mp 89–90 °C); MS *m/z* 174 ($M^+$); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ 1.97–2.04 (apparent quintet, 2H), 2.47–2.58 (m, 2H), 2.63–2.70 (m, 2H), 3.81 (s, 3H), 6.04 (m, 1H), 6.84 (d, $J$=9.3 Hz, 2H), 7.37 (d, $J$=9.3 Hz, 2H); identical to that reported.[21]

**4.7.7. 1-(4-Chlorophenyl)cyclopentene (12f).** Chromatographic solvent: PE/$Et_2O$, 9.8:0.2. GC and GC–MS analyses showed a slight contamination (2.5%) of the regioisomer 3-(4-chlorophenyl)cyclopentene (confirmed by $^1$H NMR). After crystallization from EtOH, the title compound was obtained pure: mp 73.2–73.6 (lit.[4c] mp 74–74.5 °C); MS *m/z* 178 ($M^+$); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ 1.89–2.03 (apparent quintet, 2H), 2.41–2.52 (m, 2H), 2.56–2.67 (m, 2H), 6.11 (m, 1H), 7.21 (d, $J$=8.6 Hz, 2H), 7.28 (d, $J$=8.6 Hz, 2H).

**4.7.8. 1-(4-Bromophenyl)cyclopentene (12g).** Chromatographic solvent: PE/$Et_2O$, 9.5:0.5; mp 94.6–95.4 °C, from EtOH (lit.[26] mp 97–98 °C); MS *m/z* 222 ($M^+$); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ 1.85–2.18 (apparent quintet, 2H), 2.44–2.60 (m, 2H), 2.60–2.76 (m, 2H), 6.18 (m, 1H), 7.29 (d, $J$=8.7 Hz, 2H), 7.42 (d, $J$=8.7 Hz, 2H).

**4.7.9. 1-(2-Nitrophenyl)cyclopentene (12h).** Chromatographic solvent: PE/$Et_2O$, 9:1; colorless liquid: bp 122 °C/1.5 mmHg; MS *m/z* 189 ($M^+$); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ 1.99–2.06 (apparent quintet, 2H), 2.47–2.60 (m, 4H), 5.83 (m, 1H), 7.32–7.40 (m, 2H), 7.45–7.55 (m, 1H), 7.71–7.76 (m, 1H). Anal. Calcd for $C_{11}H_{11}NO_2$ (189.21): C, 69.83; H, 5.86; N, 7.40. Found C, 69.87; H, 5.90; N, 7.43.

### 4.8. Heck-type reactions of dry arenediazonium tetrafluoroborates with ethyl acrilate (2) and cyclopentene (11); representative procedures

**4.8.1. (*E*)-Ethyl 4-nitrocinnamate (7k).** According to procedure A described above for entry 23 of Table 1, 4-nitrobenzenediazonium tetrafluoroborate[27] (0.36 g, 1.5 mmol) was added in one portion with stirring to a solution of ethyl acrilate (**2**; 0.18 g, 1.8 mmol) and $Pd(OAc)_2$ (1 mol%; 0.004 g, 0.015 mmol) in absolute EtOH (15 ml) and the reaction mixture was placed in an oil bath at 70 °C. A test of azo coupling with 2-naphthol was negative 15 min after the addition of the salt. Usual work up provided the pure (GC, GC–MS, TLC, $^1$H NMR) title compound in 93% yield (0.31 g); physical and $^1$H NMR data were identical to those of the sample reported in Section 4.3.1.

**4.8.2. (*E*)-Ethyl 4-nitrocinnamate (7k).** According to procedure B described above for entry 24 of Table 1, the above reaction mixture in 95% aqueous EtOH (15 ml) was stirred at rt until absence of azo coupling with 2-naphthol (30 min). Usual work up provided the pure (GC, GC–MS, TLC, $^1$H NMR) title compound in 100% yield (0.33 g); physical and $^1$H NMR data were identical to those of the sample reported in Section 4.3.1.

**4.8.3. (*E*)-Ethyl 2-nitrocinnamate (7j).** According to procedure A described above for entry 21 of Table 1, a mixture constituted of 2-nitrobenzenediazonium tetrafluoroborate[27] (0.36 g, 1.5 mmol), ethyl acrilate (**2**; 0.18 g, 1.8 mmol) and $Pd(OAc)_2$ (1 mol%; 0.004 g, 0.015 mmol) in absolute EtOH (15 ml) and maintained under stirring, was placed in an oil bath at 70 °C, until completion of the reaction (15 min). Usual work up provided the pure (GC, GC–MS, TLC, $^1$H NMR) title compound in 100% yield (0.33 g); physical and $^1$H NMR data were identical to those of the sample reported in Section 4.3.12.

**4.8.4. 1-(4-Tolyl)cyclopentene (12b).** According to the general procedure described above for entry 11 of Table 3, a mixture constituted of 4-toluenediazonium tetrafluoroborate[27] (0.31 g, 1.5 mmol), cyclopentene (**11**; 0.12 g, 1.8 mmol) and $Pd(OAc)_2$ (1 mol%; 0.004 g, 0.015 mmol) in aqueous 95% EtOH (15 ml), was stirred at rt until completion of the reaction (10 min; absence of azo coupling with 2-naphthol). After the usual work up, the crude residue was column chromatographed, eluting with PE/$Et_2O$, 9.8:0.2, to afford a mixture (0.21 g, 73% yield) of the title compound **12b** and the regioisomer 3-(4-tolyl)cyclopentene (confirmed by $^1$H NMR analysis), in a 94:6 GC ratio.

**4.8.5. 1-(4-Chlorophenyl)cyclopentene (12f).** The reaction was carried out as described above, starting from

4-chlorobenzenediazonium tetrafluoroborate[27] (0.34 g, 1.5 mmol) and was complete after 10 min at rt. After the usual work up, the crude residue was column chromatographed, eluting with PE/$Et_2O$, 9.5:0.5, to afford a mixture (0.19 g, 73% yield) of the title compound **12f** and the regioisomer 3-(4-chlorophenyl)cyclopentene, in a 86:14 GC ratio; $^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ 1.55–1.70 (m, 1H), 1.89–2.03 (apparent quintet, 2H), 2.30–2.41 (m, 3H), 2.41–2.52 (m, 2H), 2.56–2.67 (m, 2H), 3.73–3.88 (m, 1H), 5.67–5.71 (m, 1H), 5.89–5.92 (m, 1H), 6.11 (m, 1H), 7.06 (d, $J$=8.8 Hz, 2H), 7.20 (d, $J$=8.8 Hz, 2H), 7.21 (d, $J$=8.6 Hz, 2H), 7.28 (d, $J$=8.6 Hz, 2H).

**4.8.6. 1-(4-Nitrophenyl)cyclopentene (12i).** The reaction was carried out as described above, starting from 4-nitrobenzenediazonium tetrafluoroborate[27] (0.36 g, 1.5 mmol) and was complete after 10 min at rt. After the usual work up, the crude residue was column chromatographed, eluting with PE/$Et_2O$, 9:1, to afford a mixture (0.24 g, 84% yield) of the title compound **12i** and the regioisomer 3-(4-nitrophenyl)cyclopentene, in a 79:21 GC ratio; $^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ 1.67–1.83 (m, 1H), 1.99–2.14 (apparent quintet, 2H), 2.46–2.54 (m, 3H), 2.56–2.60 (m, 2H), 2.70–2.78 (m, 2H), 3.98–4.02 (m, 1H), 5.74–5.79 (m, 1H), 6.02–6.06 (m, 1H), 6.42 (m, 1H), 7.34 (d, $J$=8.8 Hz, 2H), 7.54 (d, $J$=8.3 Hz, 2H), 8.15 (d, $J$=8.8 Hz, 2H), 8.16 (d, $J$=8.3 Hz, 2H).

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