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Reactions of Dry Arenediazonium *o*-Benzenedisulfonimides with Triorganoindium Compounds

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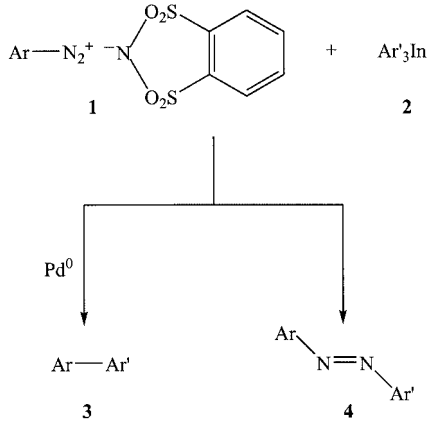
The reaction between various arenediazonium *o*-benzenedisulfonimides and triorganoindium compounds is described. Depending on the reaction conditions, it is possible to obtain biaryls (16 examples, average yield of 79%) or diaryldiazenes (18 examples, average yield of 81%). *o*-Benzenedisulfonimide can be recovered and reused to prepare additional arenediazonium *o*-benzenedisulfonimides.

Introduction

Following earlier research directed towards developing the synthetic potential of the dry, stable, arenediazonium *o*-benzenedisulfonimides **1** in Pd-catalyzed cross-coupling reactions,[1] in this paper, we have focused our attention on the reaction of these salts with triorganoindium compounds **2** in order to obtain, depending on the reaction conditions, biaryls **3** or diaryldiazenes **4**. In the presence of Pd^0 as catalyst, it was possible to achieve biaryls **3** and without catalyst, diaryldiazenes **4** (Scheme 1).



Scheme 1.

Biaryls are fundamental building blocks in organic synthesis; the biaryl unit is, in fact, present in several compounds of current interest, as in the case of natural products, polymers, advanced materials, liquid crystals, ligands and molecules of medicinal interest. As a consequence, numerous articles have dealt with interesting results in the area of aryl-aryl bond formation.[2]

The Pd-catalyzed cross-coupling reactions usually involve the coupling of an arylmetal compound with an aryl electrophile in the presence of a Pd^0 catalyst.[3] The aryl electrophile component is frequently limited to the use of halides[3] or triflates,[4] although in recent years, diazonium salts were also used as electrophilic partners.[5] Among all the possible arylmetals used as nucleophilic partners, boronic acids or their derivatives[6] (Suzuki coupling) and organotin compounds[7] (Stille coupling) found widespread synthetic application.

In recent years, in order to find new organometallic compounds useful in organic synthesis, indium organometallic compounds have been introduced.[8] They have attracted the attention of organic chemists for the ease with which they are prepared,[9] their remarkable reactivity[8] and low toxicity.[10] A wide variety of indium organometallics has been recently used in fundamental reactions of organic synthesis such as conjugate additions,[11] additions to a triple bond,[12] nucleophilic allylic substitutions[13] and cross-coupling reactions. In particular, the Pd-catalyzed cross-coupling reactions of indium organometallics with aryl halides,[14,15] aryl or vinyl triflates,[15] benzyl halides,[14] acid chlorides[14] and allylic halides or acetates[16] usually afford cross-coupling products in high yields. Furthermore, recent studies have described the use of indium organometallics in multifold and sequential cross-coupling reactions;[17] they were also employed with good results in Pd-catalyzed carbonylative cross-coupling to obtain unsymmetrical ketones.[9,18]

It must be stressed that in the literature, to our knowledge, no reactions of diazonium salts with indium organometallics have been reported.

Currently, the main method of preparing indium organometallics involves the reaction of indium(III) chloride with the readily available lithioorganic compounds or Grignard

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reagents. In this way, it is possible to obtain a large variety of indium organometallics.[9,14]

Results and Discussion

To begin with, we reacted 4-methoxybenzenediazonium *o*-benzenedisulfonimide (**1d**) with triphenylindium (**2a**) at room temperature in THF, in the presence of a catalytic amount (5%) of three different Pd catalysts and with various molar ratios. The results are listed in Table 1. Optimal reaction conditions (Entry 3) consisted of **1d/2a** in a 3:1 molar ratio and the use of bis(triphenylphosphane)palladium(II) dichloride as the precatalyst. Under these conditions, we recovered a good amount (86% yield) of 4-methoxybiphenyl (**3da**).

Table 1. Trial reactions between **1d** and **2a**.

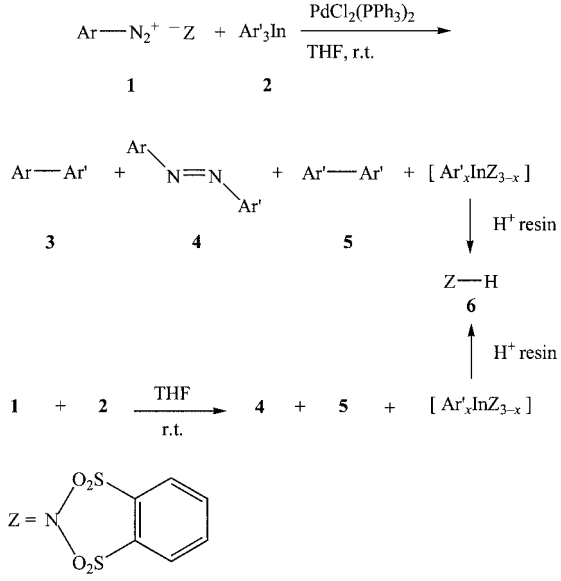
Entry	Molar ratio **1d/2a**	Reaction time [min]	Catalyst	Yield [%][a,b] **3da**	**4da**
1	1:1	30	$Pd(PPh_3)_2Cl_2$	40	14
2	2:1	15	$Pd(PPh_3)_2Cl_2$	68	14
3	3:1	5	$Pd(PPh_3)_2Cl_2$	86	5
4	3:1	5	$Pd(OAc)_2$	–	–[c]
5	3:1	10	$Pd(PPh_3)_4$	76	1

[a] Yields refer to the pure products isolated by column chromatography. The eluent was petroleum ether/diethyl ether (9:1). [b] Compound **5a** (about 6% yield) was also recovered. [c] 4-Methoxybenzene, MS (EI): m/z = 108 $[M]^+$ was detected on MS analyses but was not recovered owing to its volatility.

In light of this, it is obvious that **2a** can transfer to the salt **1d** all three groups attached to indium, unlike other organometallics usually employed in cross-coupling reactions, which can transfer only one group. These results show that indium organometallics **2** are powerful reagents in Pd-catalyzed cross-coupling reactions with diazonium salts **1** as electrophilic partners.

Moreover, in almost all the trial reactions (Table 1, Entries 1–3, 5), we also observed (*E*)-1-(4-methoxyphenyl)-2-phenyldiazene (**4da**), resulting from the electrophilic *C*-coupling reaction of **1d** with **2a**.

On these grounds, numerous variously substituted arenediazonium *o*-benzenedisulfonimides **1** were reacted with different triorganoindium compounds **2**. All the reactions were carried out in THF in the presence of a catalytic amount (5%) of bis(triphenylphosphane)palladium(II) dichloride at room temperature (Scheme 2). The results are listed in Table 2. Biaryls **3** were obtained in high yields, comparable to those reported in the literature for cross-coupling reactions between arenediazonium tetrafluoroborates and boronic acid[5a–5d] or arenediazonium *o*-benzenedisulfonimides and aryltin derivatives.[1a] The reaction is chemoselective; no trace of possible terphenyl side-products were detected in the reactions of diazonium salts bearing a halogen atom, which could potentially react with a diazonium group (Table 2, Entries 5, 6, 14, and 16). The reaction is not affected by electronic effects; biaryls **3** were obtained in high yields from the reactions of diazonium salts bearing either electron-donating or electron-withdrawing groups. On the contrary, the reaction is influenced by steric effects. In the presence of *ortho*-substituted arenediazonium *o*-benzenedisulfonimides, we observed a decrease in the yields (Table 2, Entries 2, 7, 11, and 12).



Ar in **1,3,4**	Ar in **1,3,4**	Ar' in **2,3,4,5**
a 4-MeC_6H_4	**i** 4-$NO_2C_6H_4$	**a** C_6H_5
b 2-$MeOC_6H_4$	**j** 4-$MeCOOC_6H_4$	**b** 4-$MeOC_6H_4$
c 3-$MeOC_6H_4$	**k** 2,6-$F_2C_6H_3$	**c** 4-ClC_6H_4
d 4-$MeOC_6H_4$	**l** 2,6-$(NO_2)_2C_6H_3$	**d** 4-MeC_6H_4
e 4-BrC_6H_4	**m** 4-ClC_6H_4	**e** 2-thienyl
f 4-IC_6H_4	**n** 3-BrC_6H_4	
g 2-$NO_2C_6H_4$	**o** 4-CNC_6H_4	
h 3-$NO_2C_6H_4$	**p** 2,6-$(Me)_2C_6H_3$	

Scheme 2.

The catalytic cycle of the reaction, similar to those previously reported in the literature,[1a,5b,5e,7b] is summarized in Scheme 3 and can be described in four steps: 1) formation of Pd^0; 2) oxidative addition; 3) transmetallation and 4) reductive elimination. In order to simplify Scheme 3, please note that we did not mark the ligands of bis(triphenylphosphane)palladium(II) dichloride, and we illustrated compound **2** transferring only one group to the diazonium salt **1**.

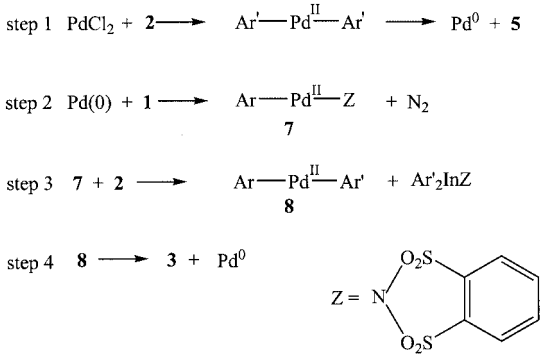
It must again be stressed that, in all the reactions listed in Table 2, some amounts of diaryldiazenes **4** were always recovered. On these grounds, we decided to react arenediazonium *o*-benzenedisulfonimides **1** with triorganoindium compounds **2** without catalysts in order to favour the electrophilic *C*-coupling reaction and maximize the yields of diaryldiazenes **4** (Scheme 2).

Also, we performed some preliminary experiments in order to optimize the reaction. We reacted **1d** with **2a** in different molar ratios at room temperature in THF. The results are reported in Table 3. Under the best conditions (Entry 5), the molar ratio between **1d** and **2a** was 1:2, in contrast to the 3:1 ratio previously used in the Pd-catalyzed reactions.

Table 2. Biaryl compounds **3**.

Entry		Ar	Ar′	Yield [%][a–c]		Biaryl compounds **3**		
				3	**4**	MS (EI): *m/z* $[M]^+$	M.p.[d] or b.p. (°C/Torr)	Lit. m.p or b.p (°C/Torr)
1	**3aa**	4-MeC_6H_4	C_6H_5	94	tr.[e]	168	47–48	46–47[20]
2	**3ba**	2-$MeOC_6H_4$	C_6H_5	74	3	184	31–32	29[21]
3	**3ca**	3-$MeOC_6H_4$	C_6H_5	80	3	184	82–83/0.5	140/5[21]
4	**3da**	4-$MeOC_6H_4$	C_6H_5	86	5	184	88–89	89[21]
5	**3ea**	4-BrC_6H_4	C_6H_5	86	3	232	91–92	90[21]
6	**3fa**	4-IC_6H_4	C_6H_5	85	3	280	110–111	112–113[5b]
7	**3ga**	2-$NO_2C_6H_4$	C_6H_5	70	2	199	38–39	37[21]
8	**3ha**	3-$NO_2C_6H_4$	C_6H_5	85	1	199	59–60	59[21]
9	**3ia**	4-$NO_2C_6H_4$	C_6H_5	89	4	199	115–116	113[21]
10	**3ja**	4-$MeCOOC_6H_4$	C_6H_5	94	tr	212	116–117	115–116[20]
11	**3ka**	2,6-$F_2C_6H_3$	C_6H_5	74	3	190	97–98	93[22]
12	**3la**	2,6-$(NO_2)_2C_6H_3$	C_6H_5	21	1[f]	244	190–191	189–191[23]
13	**3ab**	4-MeC_6H_4	4-$MeOC_6H_4$	79	tr.[e]	198	109–110	110[24]
14	**3mb**	4-ClC_6H_4	4-$MeOC_6H_4$	84	tr.[e]	268	110–111	110–111[25]
15	**3ib**	4-$NO_2C_6H_4$	4-$MeOC_6H_4$	88	tr.[e]	229	110–111	109–110[26]
16	**3ec**	4-BrC_6H_4	4-ClC_6H_4	82	tr.[e]	266	157–158	157–158[27]

[a] The reaction time was 5 min for all reactions. [b] Yields refer to the pure products, isolated by column chromatography. The eluent was always petroleum ether/diethyl ether (9:1). [c] In Entries 1–12, compound **5a** (about 6% yield) was also recovered. In Entries 13–15, a trace of compound **5b** {MS (EI): *m/z* = 214 $[M]^+$} was detected upon MS analyses. In Entry 16, a trace of compound **5c** {MS (EI): *m/z* = 222 $[M]^+$} was detected upon MS analyses. [d] Crystallization solvent: MeOH. [e] tr. = trace. [f] 1,3-Dinitrobenzene {0.30 g, 12%, MS(EI): *m/z* = 168 $[M]^+$} was also recovered.



Scheme 3.

Table 3. Trial reactions between **1d** and **2a** without catalyst.

Entry	Molar ratio **1d/2a**	Reaction time [min]	Yield [%][a,b] **4da**
1	3:1	60	16
2	2:1	60	42
3	1:1	45	53
4	1:1.5	30	66
5	1:2	10	93

[a] Yields refer to the pure products, isolated by column chromatography. The eluent was petroleum ether/diethyl ether (9.5:0.5). [b] Compound **5a** (about 5% yield) was also recovered.

Having found the optimal reaction conditions, we tested the reaction between various arenediazonium *o*-benzenedisulfonimides **1** and triorganoindium compounds **2**, obtaining diaryldiazenes **4** in good yields, as reported in Table 4. Therefore, this reaction represents an efficient procedure for the preparation of variously functionalized diaryldiazenes **4**, and the results obtained with triorganoindium compounds **2** are comparable to those previously described by our laboratory[19] in the electrophilic *C*-coupling reaction of arenediazonium *o*-benzenedisulfonimides with Grignard reagents.

Note that it was possible to recover *o*-benzenedisulfonimide (**6**) in more than 80% yield from all the reactions described heretofore. The product **6** probably derived from hypothetical intermediates Ar'_xInZ_{3-x}, which are shown in brackets in Scheme 2, but were never detected spectroscopically. *o*-Benzenedisulfonimide (**6**) could be recycled for the preparation of other salts **1** (Scheme 2).

To understand the behaviour of arenediazonium *o*-benzenedisulfonimides **1** in the reactions with triorganoindium compounds **2**, we used organometallic compounds other than **2a** including tributylphenyltin (**9a**), phenylboronic acid (**9b**), phenylmagnesium bromide (**9c**) and phenyllithium (**9d**) and performed reactions with or without Pd^0 catalyst (Scheme 4). The results are reported in Table 5.

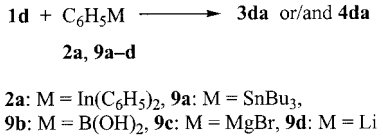
The results can be explained by the different nucleophilicity of compounds **9**. In fact, **9a** and **9b** are too weakly nucleophilic to react with **1d** in the absence of Pd^0 (Table 5, Entries 1 and 3). The reaction with **1d** occurred only in the presence of the catalyst with the formation of the cross-coupling product **3da** (Table 5, Entries 2 and 4). The Grignard reagent **9c** is a stronger nucleophile than **9a** or **9b** and reacted with **1d** to afford **4da** by electrophilic *C*-coupling (Table 5, Entry 7). This reaction is probably faster than the oxidative addition (the second step in the catalytic cycle), and the only product formed in the presence or absence of Pd^0 was **4da** (Table 5, Entry 8).

Because **2a** is a stronger nucleophile than **9a** or **9b** but weaker than **9c**, only a large excess of it afforded **4da** (Table 5, Entry 5). On the contrary, with a large excess of **1d** and Pd^0 as the catalyst (Table 5, Entry 6), the main prod-

Table 4. Diaryildiazenes **4**.

Entry		Ar	Ar′	Solvent[a] for chromatography	Yield [%][b–d] **4**	MS (EI) *m/z* [M$^+$]	Diaryldiazenes **4** M.p.[e,f] or b.p. (°C/Torr)	Lit. m.p. or b.p. (°C/Torr)
1	**4aa**	4-MeC_6H_4	C_6H_5	PE/EE (9.9:0.1)	95	196	71–72	71–72[19]
2	**4ba**	2-MeOC_6H_4	C_6H_5	PE/EE (9.5:0.5)	81	212	38–39	41[28]
3	**4ca**	3-MeOC_6H_4	C_6H_5	PE/EE (9.5:0.5)	90	212	31–32	31–32[19]
4	**4da**	4-MeOC_6H_4	C_6H_5	PE/EE (9.5: 0.5)	90	212	53–54	53–54[19]
5	**4ea**	4-BrC_6H_4	C_6H_5	PE	90	260	88–89	88–89[19]
6	**4fa**	4-IC_6H_4	C_6H_5	PE	90	308	105–106	105[29]
7	**4ga**	2-$NO_2C_6H_4$	C_6H_5	PE/EE (9.5:0.5)	88	227	69–70	67–68[30]
8	**4ha**	3-$NO_2C_6H_4$	C_6H_5	PE/EE (9.5:0.5)	90	227	95–96	96[31]
9	**4ia**	4-$NO_2C_6H_4$	C_6H_5	PE/EE (9.5:0.5)	90	227	132–133	133[32]
10	**4ja**	4-MeCOOC_6H_4	C_6H_5	PE/EE (9.1)	81	240	125–126	126–127[33]
11	**4ka**	2,6-$F_2C_6H_3$	C_6H_5	PE	96	218	81–82	80–82[34]
12	**4la**	2,6-$(NO_2)_2C_6H_3$	C_6H_5	PE/EE (9.5:0.5)	66[g]	272	129–131	[h]
13	**4pa**	2,6-$(Me)_2C_6H_3$	C_6H_5	PE/EE (9.9:0.1)	43	210	139/0.8	160/10[35]
14	**4ed**	4-BrC_6H_4	4-MeC_6H_4	PE	84	274	151–152	151–152[19]
15	**4nd**	3-BrC_6H_4	4-MeC_6H_4	PE	76	274	120–121	120–121[19]
16	**4ec**	4-BrC_6H_4	4-ClC_6H_4	PE	81	294	192–193	192–193[19]
17	**4mc**	4-ClC_6H_4	4-ClC_6H_4	PE	80	250	188–189	188–189[19]
18	**4oe**	4-CNC_6H_4	2-thienyl	PE/EE (9.5:0.5)	47	213	182–183	[h]

[a] PE = Petroleum ether; EE = Diethyl ether. [b] The reaction time was 10 min for all reactions. [c] Yields refer to pure products, isolated by column chromatography. [d] In Entries 1–13, compound **5a** (about 5% yield) was also recovered. In Entries 14 and 15, a trace of compound **5d** {MS (EI): *m/z* = 182 [M]$^+$} was detected upon MS analyses. In Entries 16 and 17, a trace of compound **5c** {MS (EI): *m/z* = 222 [M]$^+$} was detected upon MS analyses. In Entry 18, a trace of compound **5e** {MS (EI): *m/z* = 166 [M]$^+$} was detected upon MS analyses. [e] Crystallization solvent: MeOH. [f] M.p. of compounds **4aa**–**4fa**, **4ia**, **4ja**, and **4pa**–**4mc** are identical to those reported in the literature for diaryldiazenes in the *E* form. Therefore an *E* form is presumable also for all the other diaryldiazenes. [g] 2-Chloro-1,3-dinitrobenzene {0.20 g, 20%, MS (EI): *m/z* = 202 [M]$^+$} was also recovered. [h] Products **4la** and **4oe** are unknown in the literature.



Scheme 4.

Table 5. Reaction between **1d** and various organometallics **2a**, **9a**–**d**.

Entry	Organometallic **2a**, **9a**–**d**	Catalyst	Yield [%][a] **3da**	**4da**
1	$C_6H_5SnBu_3$ (**9a**)	–	–	–[b]
2	$C_6H_5SnBu_3$ (**9a**)	$Pd(OAc)_2$	81	–
3	$C_6H_5B(OH)_2$ (**9b**)	–	–	–[b]
4	$C_6H_5B(OH)_2$ (**9b**)	$Pd(OAc)_2$	82	–
5	$(C_6H_5)_3In$ (**2a**)	–	–	90
6	$(C_6H_5)_3In$ (**2a**)	$Pd(PPh_3)_2Cl_2$	86	5
7	C_6H_5MgBr (**9c**)	–	–	80
8	C_6H_5MgBr (**9c**)	$Pd(PPh_3)_2Cl_2$	–	75
9	C_6H_5Li (**9d**)	–	–	–[c]
10	C_6H_5Li (**9d**)	$Pd(PPh_3)_2Cl_2$	–	–[c]

[a] Yields refer to the pure products, isolated by column chromatography. The eluent was petroleum ether/diethyl ether (9:1). [b] The unreacted salt **1d** was recovered at the reaction end. [c] The presence of 4-methoxybenzene {MS (EI): *m/z* = 108 [M]$^+$} was detected upon MS analyses.

uct was **3da**. Under these conditions, the oxidative addition prevailed over the electrophilic *C*-coupling reaction. Finally, the very strong nucleophile **9d** caused mainly the decomposition of **1d** (Table 5, Entries 9 and 10).

Conclusions

In conclusion, the importance and synthetic utility of the reaction between arenediazonium *o*-benzenedisulfonimides **1** and indium organometallic compounds **2** can be schematized in the following points: *i*) the use of diazonium salts as electrophiles instead of the corresponding aryl halides or triflates. In fact, there are many advantages associated with diazonium salts, particularly their greater reactivity, due to the fact that the diazonium group is a better nucleofuge than the halide or triflate. Moreover, the use of the arenediazonium *o*-benzenedisulfonimides **1** has several advantages over the use of other diazonium salts, including high stability, ease of preparation and the possibility of recovering *o*-benzenedisulfonimide at the end of the reaction, Furthermore, unlike other acids (e.g. tetrafluoroboric acid), *o*-benzenedisulfonimide is a non-risk acid that can be reused to prepare other salts, with ecological and economic advantages. *ii*) the use of triorganoindium compounds. These compounds are easy to prepare, extremely reactive and exhibit little or no toxicity. Moreover, these compounds can transfer to the diazonium salt all three groups attached to indium, unlike other organometallics used in cross-coupling reactions that can transfer only one group. *iii*) it is possible to obtain two different products (biaryls **3** or diaryldiazenes **4**) in high yields, depending on the reaction conditions.

Experimental Section

General Remarks: 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 40–70 °C. ^{1}H NMR spectra were recorded with a Bruker Avance 200 spectrometer. Mass spectra were recorded with an HP 5989B mass-selective detector connected to an HP 5890 GC, with a cross-linked methyl silicone capillary column. Room temperature is 20–25 °C. Chromatographic solvent, yields and physical and spectroscopic data (MS) of the pure (GC, GC-MS, TLC and ^{1}H NMR) isolated biaryls **3** and diaryldiazenes **4** are reported in Table 2 and Table 4. Structures and purities of all the products obtained in this research were confirmed by comparison of their physical (m.p. or b.p.) and spectroscopic data with those reported in the literature.

Indium(III) chloride, phenyllithium (1.9 M solution in butyl ether), 2-thienyllithium (1.0 M solution in THF), phenylmagnesium bromide (1 M solution in THF), 4-methoxyphenylmagnesium bromide (0.5 M solution in THF), 4-tolylmagnesium bromide (1.0 M solution in THF), 4-chlorophenylmagnesium bromide (1.0 M solution in diethyl ether), palladium(II) acetate, tetrakis(triphenylphosphane)-palladium(0), bis(triphenylphosphane)palladium(II) dichloride and all of the amines and solvents were purchased from Aldrich. Dowex 50X8 ion-exchange resin was purchased from Fluka.

Dry arenediazonium *o*-benzenedisulfonimides **1** were prepared as described previously.[1] The crude salts were virtually pure (by ^{1}H NMR spectroscopy) and were used in subsequent reactions with indium organometallics **2** without further crystallization.

CAUTION! In our laboratory there 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.

Triorganoindium Compounds 2. General Procedure: As reported in the literature,[9] a solution of indium(III) chloride (1.11 g, 5 mmol) in dry THF (20 mL) was cooled to 0 °C under N_2 flow.

A suitable Grignard reagent or aryllithium derivative (15 mmol) was added dropwise over a period of 10 min. Stirring was continued at 0 °C for 45 min until the formation of triarylindium derivatives was complete. In this way, triphenylindium (**2a**), tris(4-methoxyphenyl)indium (**2b**), tris(4-chlorophenyl)indium (**2c**), tris(4-methylphenyl)indium (**2d**) and tri(2-thienyl)indium (**2e**) were synthesized and used directly, without isolation, in the subsequent step.

4-Methoxybiphenyl (3da). Typical Procedure: To a solution of triphenylindium (**2a**, 5 mmol in THF, prepared as previously reported), were added with vigorous stirring in one portion and at room temperature, bis(triphenylphosphane)palladium(II) dichloride (0.17 g, 0.25 mmol) and 4-methoxybenzenediazonium *o*-benzenedisulfonimide (**1d**, 15 mmol, 5.29 g). The salt dissolved at once, and the resulting solution became deep orange. Stirring was maintained for 5 min at room temperature. The completion of the reaction was confirmed by the absence of azo coupling with 2-naphthol. GC, GC-MS and TLC (petroleum ether/diethyl ether, 9:1) analyses of the reaction mixture showed 4-methoxybiphenyl {**3da**, MS (EI): m/z = 184 $[M]^+$} as the major product, besides biphenyl {**5a**, MS (EI) m/z = 154 $[M]^+$} and (*E*)-1-(4-methoxyphenyl)-2-phenyldiazene {**4da**, MS (EI): m/z = 212 $[M]^+$} as minor products. The reaction mixture was poured into diethyl ether/water (100 mL, 1:1). The aqueous layer was separated and extracted with diethyl ether (2 × 50 mL). The combined organic extracts were washed with water (2 × 50 mL), dried with Na_2SO_4 and evaporated under reduced pressure. The crude residue was chromatographed on a short column, eluting with petroleum ether/diethyl ether (9:1). The first-eluted product was biphenyl (**5a**, 0.05 g, 6% yield). The second-eluted product was the pure (GC, GC-MS, TLC and ^{1}H NMR) title compound **3da** (2.46 g, 89% yield). The third-eluted product was (*E*)-1-(4-methoxyphenyl)-2-phenyldiazene (**4da**, 0.15 g, 5% yield).

The aqueous layer and aqueous washings were collected and evaporated under reduced pressure. The black tarry residue was passed through a column of Dowex 50X8 ion exchange resin (1.6 g/1 g of product), eluting with water (about 50 mL). After removal of the water under reduced pressure, virtually pure (^{1}H NMR) *o*-benzenedisulfonimide (**6**) was recovered (2.60 g, 79% yield). M.p. 192–194 °C (toluene) (lit.[1] m.p. 192–194 °C). All the biaryls **3** reported in Entries 1–16 of Table 2 were prepared according to the above procedure.

(*E*)-1-(4-Methoxyphenyl)-2-phenyldiazene (4da). Typical Procedure: According to the above procedure, to a solution of triphenylindium (**2a**, 10 mmol in THF) at room temperature was added in one portion, with vigorous stirring, 4-methoxybenzenediazonium *o*-benzenedisulfonimide (**1d**, 5 mmol, 1.76 g). The salt dissolved at once, and the resulting solution became very dark. Stirring was maintained for 10 min at room temperature until a test of azo coupling with 2-naphthol was negative. GC, GC-MS and TLC (petroleum ether/diethyl ether, 9:1) analyses of the reaction mixture showed (*E*)-1-(4-methoxyphenyl)-2-phenyldiazene {**4da**, MS (EI): m/z = 212 $[M]^+$} as the major product, besides biphenyl {**5a**, MS (EI): m/z = 154 $[M]^+$} as the minor product. The above workup furnished a crude residue that was chromatographed on a short column, eluting with petroleum ether/diethyl ether (9:1). The first-eluted product was biphenyl (**5a**, 0.07 g, 5% yield). The second-eluted product was the pure (GC, GC-MS, TLC and ^{1}H NMR) title compound (**4da**, 0.95 g, 90% yield). All the diaryldiazenes **4** reported in Entries 1–18 of Table 4 were prepared according to the above procedure. The structure of products **4aa**–**4ka** and **4pa**–**4mc** were confirmed by comparison of their physical (m.p. or b.p.) and spectroscopic data (^{1}H NMR) with those reported in the literature. Products **4la** and **4oe** were previously unknown.

Virtually pure (^{1}H NMR) *o*-benzenedisulfonimide (**6**) was recovered (0.83 g, 76% yield), according to the above procedure.

(*E*)-1-(2,6-Dinitrophenyl)-2-phenyldiazene (4la): ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.50–7.62 (m, 3 H), 7.65–7.70 (m, 1 H), 7.86–7.92 (m, 2 H) 8.12–8.17 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 124.0, 126.9, 129.7, 131.5, 132.4, 142.9, 143.8, 152.1 ppm. $C_{12}H_8N_4O_4$ (272.22): calcd. C 52.95; H 2.96; N 20.58; found C 52.86; H 2.85; N 20.60.

(*E*)-4-(2-Thienyldiazenyl)benzonitrile (4oe): ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.18–7.23 (m, 1 H), 7.52 (d, J = 5.31 Hz, 1 H), 7.77 (d, J = 6.19 Hz, 2 H) 7.88–7.94 (m, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 113.1, 116.2, 126.1, 126.3, 126.9, 127.5, 130.2, 132.9, 133.9 ppm. $C_{11}H_7N_3S$ (213.26): calcd. C 61.95; H 3.31; N 19.70; S 15.03; found C 61.89; H 3.33; N 19.72; S 15.04.

Trial Reactions: (a) All the reactions reported in Table 1 (Entries 1–5) were carried out according to the general procedure described above, reacting 4-methoxybenzenediazonium *o*-benzenedisulfonimide (**1d**) with triphenylindium (**2a**, 5 mmol) at room temperature, varying the catalyst and the **1d**/**2a** molar ratios. The crude residues were chromatographed on a short column, eluting with petroleum ether/diethyl ether (9:1). Details are shown in Table 1. (**b**) All the reactions reported in Table 3 (Entries 1–5) were carried out according to the general procedure described above, reacting 4-methoxybenzenediazonium *o*-benzenedisulfonimide (**1d**) with triphenylindium (**2a**, 5 mmol) at room temperature, varying the **1d**/**2a** molar ratios. The crude residues were chromatographed on a short col-

umn, eluting with petroleum ether/diethyl ether (9:1). Details are shown in Table 3.

Collateral Proofs: (a) To a solution of tributylphenyltin (**9a**, 5.5 mmol, 2.02 g) or phenylboronic acid (**9b**, 5.5 mmol, 0.61 g) in THF (20 mL) was added, under vigorous stirring in one portion and at room temperature, 4-methoxybenzenediazonium *o*-benzenedisulfonimide (**1d**, 5 mmol, 1.77 g). The obtained suspension was stirred at room temperature for 24 h; a test of azo coupling with 2-naphthol was positive. The suspension was heated at reflux for 8 h, but a test of azo coupling was still positive. The unreacted 4-methoxybenzenediazonium *o*-benzenedisulfonimide (**1d**) was recovered by filtration through a Buchner funnel (Table 5, Entries 1 and 3). (**b**) 4-methoxybiphenyl (**3da**) was obtained, as reported in the literature[1a,5a] (Table 5, Entries 2 and 4). (**c**) (*E*)-1-(4-methoxyphenyl)-2-phenyldiazene (**4da**) was obtained, as reported in the literature[19] (Table 5, Entry 7). (**d**) To phenylmagnesium bromide (**9c**, 1 M solution in THF, 5.5 mmol, 5.5 mL) was added THF (20 mL). Bis(triphenylphosphane)palladium(II) dichloride (0.17 g, 0.25 mmol) and 4-methoxybenzenediazonium *o*-benzenedisulfonimide (**1d**, 5 mmol, 1.77 g) were added at room temperature with vigorous stirring in one portion. The salt dissolved at once, and the resulting solution became very dark. Stirring was maintained for 50 min at room temperature until a test of azo coupling with 2-naphtol was negative. GC, GC-MS and TLC (petroleum ether/diethyl ether, 9:1) analyses of the reaction mixture showed (*E*)-1-(4-methoxyphenyl)-2-phenyldiazene {**4da**, MS (EI): *m*/*z* = 212 $[M]^+$} as the major product, besides 4-methoxybenzene {MS (EI): *m*/*z* = 108 $[M]^+$} as the minor product. The usual workup afforded pure (*E*)-1-(4-methoxyphenyl)-2-phenyldiazene (**4da**, 0.80 g, 75% yield). The same results were obtained with palladium(II) acetate as the catalyst (Table 5, Entry 8). (**e**) To phenyllithium (**9d**, 1.9 M solution in butyl ether, 5.5 mmol, 2.9 mL) was added THF (20 mL). Bis(triphenylphosphane)palladium(II) dichloride (0.17 g, 0.25 mmol) and 4-methoxybenzenediazonium *o*-benzenedisulfonimide (**1d**, 5 mmol, 1.77 g) were added at 0 °C with vigorous stirring in one portion. The salt dissolved at once, and the resulting solution became very dark. Stirring was maintained for 5 min at room temperature until a test of azo coupling with 2-naphtol was negative. GC, GC-MS and TLC (petroleum ether/diethyl ether, 9:1) analyses of the reaction mixture showed the presence of 4-methoxybenzene as the only product. After the usual workup only tars were recovered. The same results were obtained with palladium(II) acetate as the catalyst (Table 5, Entry 9) and without catalyst (Table 5, Entry 10).

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