1-Aryl-3,3-dialkyltriazenes: A Convenient Synthesis from Dry Arenediazonium *o*-Benzenedisulfonimides – A High Yield Break Down to the Starting Dry Salts and Efficient Conversions to Aryl Iodides, Bromides and Chlorides

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Abstract: This research comprises three parts. The first part regards the synthesis of 1-aryl-3,3-dialkyltriazenes **3** by reaction of dry arenediazonium *o*-benzenedisulfonimides **1**, also coming from weakly basic aromatic amines with dimethylamine or diethylamine in aqueous solution at 0–5 °C. Yields were usually greater than 90% and there was the possibility of recovering the *o*-benzenedisulfonimide (**5**), which could be reused to prepare the salts **1**. In the second part it was demonstrated that there is the possibility of reconverting the triazenes **3** into the starting stable dry salts **1** by using **5** as acid. The reactions were carried out in glacial acetic acid at 50–55 °C and normally afforded salts **1** in yields of around 90–99%. The third part concerns the setting up of two procedures for the conversion of **3** to aryl iodides **9**, bromides **10** and chlorides **11**. Procedure A used the corresponding aqueous hydrogen halides in acetonitrile at r.t. or 60 °C, sometimes in the presence of aqueous HBF_4, sometimes Cu powder (25 examples, yields 65%-88%). Procedure B usually used anhydrous methanesulfonic acid and tetraalkylammonium halides in anhydrous acetonitrile at temperatures varying from r.t. to 80 °C, sometimes in the presence of Cu (16 examples, yields 65–88%).

Key words: stable dry arenediazonium salts, triazenes, retro reactions, radical reactions, aryl halides

Triazenes are a class of compounds of great interest.[1] Their biological activity has been and still is, the subject of numerous studies; several triazenes are chemotherapeutic agents active against bacterial and especially, protozoal infections, while the 1-aryl-3,3-dimethyltriazenes possess significant in vivo anti-tumor activity. For example, wide therapeutic use is made of dacarbazine, i.e. 5-(3,3-dimethyltriazeno)imidazole-4-carboxamide, as an active principle against human malignant melanoma. Still in the medical field, triazenes are used in the preparation of radiolabeled materials, used as tracers in diagnostic procedures. In technological applications, the ability of triazenes to break down to yield, in situ, diazonium ions with coupling properties is widely used to produce insoluble azo dyes directly on natural and synthetic fibres. Finally, the triazene group plays a significant role in organic synthesis, being a protected form for both the diazonium group and hence for all the functional groups deriving from it and for the aromatic and aliphatic amines from which it arose.

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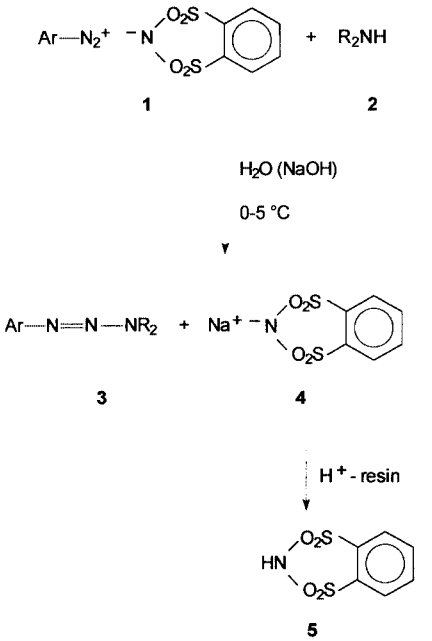
It was within a wider investigation aimed at evaluating the synthetic potential of the dry arenediazonium *o*-benzenedisulfonimides[2] **1** that the present research was undertaken, it consists of three parts: i) the setting up, based on the use of dry arenediazonium *o*-benzenedisulfonimides **1**, of a simple synthetic procedure for 1-aryl-3,3-dialkyltriazenes **3**, also valid for the preparation of unknown or difficult to obtain compounds; ii) break down of the triazenes **3** to the starting dry salts **1**; iii) realisation of efficient procedures for converting, in aqueous or anhydrous organic solvents, the 1-aryl-3,3-dialkyltriazenes **3** into aryl iodides, bromides and chlorides, via the corresponding arenediazonium salt intermediates.

With regard to 1-aryl-3,3-dialkyltriazenes synthesis, it must first be said that numerous derivatives are known and in most cases, there is no great difficulty in obtaining them through the reaction of arenediazonium salts with secondary aliphatic amines or cyclic amines like pyrrolidine or piperidine. Nevertheless there are several cases where the synthesis of the 1-aryl-3,3-dialkyltriazenes is quite troublesome. This is especially so when the diazonium salts used come from weakly basic aromatic amines, particularly nitroanilines or polyhalogenoanilines, that can be diazotised only in very harsh conditions, which has been optimised to obtain specific salts.[3] This said, we believe it useful to develop a general method for the synthesis of 1-aryl-3,3-dialkyltriazenes **3**, the method being based on the preliminary preparation of dry arenediazonium *o*-benzenedisulfonimides **1** and a subsequent reaction with aliphatic dialkylamines. The dry arenediazonium salts **1a**–**l** were easily prepared following a general method we had already developed and used to obtain many salts.[4] This method is extremely simple and fast and involves the diazotization of primary aromatic amines with *i*-pentyl nitrite in the presence of *o*-benzenedisulfonimide (**5**) in glacial acetic acid (or formic acid) at 0–5 °C and the isolation, by filtration, of the virtually pure salts that precipitate from the reaction medium. Like all the previously prepared arenediazonium *o*-benzenedisulfonimides, also the new dry salts **1f**,**h**–**l** are obtained pure and in excellent yields. They are extremely stable and can be safely stored, ready for use, for unlimited times.

The 1-aryl-3,3-dialkyltriazenes **3a**–**l** (R = Me, Et) were prepared by reacting, at 0–5 °C, the salts **1a**–**l** with dimethylamine or diethylamine **2** in aqueous solution, in the

presence of sodium hydroxide (molar ratio **1**:**2**:NaOH = 1:1.1:1) or absence (molar ratio **1**:**2** = 1:2.2) (Scheme 1). The reactions went rapidly to completion and the yields of the triazenes, virtually pure at the moment of isolation or easily purified by column chromatography, were always very high, usually greater than 90% (Table 1). A relevant advantage of the procedure is the possibility of recovering the *o*-benzenedisulfonimide (**5**) that can be reused to prepare the salts **1**, the recovery yields being between 88 and 99%.



1	Ar	1	Ar
a	4-$MeOC_6H_4$	**g**	2,4-$(O_2N)_2C_6H_3$
b	4-ClC_6H_4	**h**	2,4,6-$Cl_3C_6H_2$
c	4-$O_2NC_6H_4$	**i**	2,4,6-$Br_3C_6H_2$
d	2,6-$Cl_2C_6H_3$	**j**	2,6-Br_2-4-FC_6H_2
e	2,6-$Br_2C_6H_3$	**k**	2,6-Cl_2-4-$O_2NC_6H_2$
f	2-Cl-4-$O_2NC_6H_3$	**l**	2,6-Br_2-4-$O_2NC_6H_2$

Scheme 1

Relative to the break down of 1-aryl-3,3-dialkyltriazenes **3** to the starting dry salts **1**, it was our intent to demonstrate the possibility of reconverting the triazenes to dry stable diazonium salts. As emphasised above, the triazenes constitute a protected form of the diazonium group.[1] In fact the triazene moiety combines extreme resistance to basic hydrolysis with resistance to oxidants (PDC, H_2O_2, peracids), metal hydrides ($LiAlH_4$, $NaBH_4$), hydrogenation (Pd/C in MeOH), alkylating agents (MeI at r.t.), alkyl lithium and lithium amide bases (*s*-BuLi, *t*-BuLi, LDA) and Lewis acids ($Ti(Oi\text{-}Pr)_4$).[5,6] Consequently, numerous reactions can be carried out on substrates containing the triazene group, without any effect whatever on the functional group itself. When necessary the triazene can be reconverted to the diazonium salts, allowing further reaction. Nevertheless, to the best of our knowledge, in all the cases reported in the literature, with only two exceptions (i.e., 4-toluenediazonium trifluoroacetate and trifluoromethanesulfonate),[7] the diazonium salts obtained from the triazenes were not isolated, but were left to react directly in situ. Such methodology limits the synthetic potential of diazonium salts obtained from triazenes, in that deprotection is normally carried out with acids and the resultant reaction medium can thus become incompatible for subsequent in situ reactions. On the contrary, after carrying out the desired reactions on substrates containing the triazene moiety, the modified triazenes are converted to the stable dry diazonium salts, they are able to fully express their synthetic potential. The present work achieved this goal. In fact, the triazenes **3** were easily reconverted to the corresponding dry arenediazonium *o*-benzenedisulfonimides **1**, simply by adding them to a solution of the *o*-benzenedisulfonimide (**5**) (molar ratio **1**:**5** = 1:2.2) in glacial acetic acid or acetic acid–formic acid (9.7:0.3), maintained at 50–55 °C for 15–30 min. On cooling the reaction mixture to 20–25 °C, the arenediazonium *o*-benzenedisulfonimides **1** precipitated spontaneously and could be collected by filtration, normally in yields of around 90% to 99% (Experimental Section). High yields of the *o*-benzenedisulfonimide (**5**) were easily recovered from the acetic solution containing the dialkylammonium salts. The only negative result concerned the triazene **3g**.

With regard to the conversion of triazenes to aryl halides, it must be noted that most of the work reported in the literature has been principally aimed at the preparation of aryl iodides;[8] little attention has been paid to aryl bromides[6,8b,9,10] and aryl chlorides are dealt with only exceptionally.[6] The most significant procedures for the conversion of the 1-aryl-3,3-dialkyltriazenes to aryl iodides takes the following routes: i) break down of **3** with aqueous hydrochloric acid or trifluoroacetic acid in the presence of potassium iodide (5 examples, isolated product yields: 51–66%);[8a] ii) conversion by the action of iodotrimethylsilane in acetonitrile (4 examples, isolated product yields: 65–92%);[8b] iii) treatment with sodium iodide and a sulfonic acid cation-exchange resin in anhydrous acetonitrile (10 examples, isolated product yields 72–95%);[8c] iv) treatment with methyl iodide in a sealed tube at 100–120 °C (9 examples, G.C. or isolated product yields > 94%);[8d] v) iodine-promoted decomposition in a sealed tube at 80–100 °C in different solvents (6 examples, G.C. yields: 85–98%).[8e] Considering the various procedures developed in the past we have, to some extent, been surprised by the fact that there is no mention in the literature of the possibility of converting 1-aryl-3,3-dialkyltriazenes to aryl iodides simply by aqueous hydroiodic acid treatment. Available to us was the series of the 1-aryl-3,3-dialkyltriazenes **3a–l** where, in most cases, the presence of electron withdrawing groups on the aryl makes conversion to aryl iodides via diazonium cations difficult; this prompted us to attempt the conversion of such triazenes by treating them with aqueous hydroiodic acid. This was not so simple and in reality, we had to carry out many

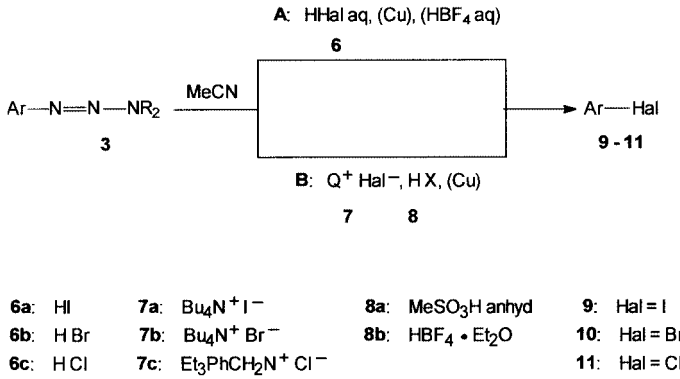
Table 1 1-Aryl-3,3-dialkyltriazenes **3a –l**

Compd.[a]	Ar	R	Chromatographic solvent[d]	Yield[b] (%)	Mp[c] (°C) or bp (°C)/mbar	MS *m*/z (M^+)	Yield (%) of **5** recovered	^{1}H NMR ($CDCl_3$) δ (ppm), *J* (Hz)
3a	4-$MeOC_6H_4$	Me	PE–Et_2O (9:1)	91	141–142/1.5[e]	179	92	[f]
3b	4-ClC_6H_4	Me	PE–Et_2O (9:1)	90	55.6–56.8[e]	183	98	[f]
3c	4-$O_2NC_6H_4$	Me	$CHCl_3$	86	142.6–143.7[e]	194	96	[f]
3d	2,6-$Cl_2C_6H_3$	Et	[g]	90[h]	155/4.7×10^{-3}	245	97	1.31 (t, 6 H, *J* = 7.1), 3.79 (q, 4 H, *J* = 7.1), 6.97 (t, 1 H, *J* = 7.9), 7.29 (d, 2 H, *J* = 7.9)
3e	2,6-$Br_2C_6H_3$	Et	[g]	95[h]	35.9–36.5	333	94	1.35 (t, 6 H, *J* = 7.1), 3.80 (q, 4 H, *J* = 7.1), 6.82 (t, 1 H, *J* = 7.9), 7.52 (d, 2 H, *J* = 7.9)
3f	2-Cl-4-$O_2NC_6H_3$	Et	C–Et_2O (9.6:0.4)	91	59.0–59.4	256	89	1.35 (t, 6 H, *J* = 7.1), 3.88 (q, 4 H, *J* = 7.1), 7.52 (d, 1 H, *J* = 8.0), 8.10 (dd, 1 H, *J* = 8.0, 2.0) 8.30 (d, 1 H, *J* = 2.0)
3g	2,4-$(O_2N)_2C_6H_3$	Me	[g]	94[h]	131.0–132.2	239	88	3.30 (s, 3 H), 3.75 (s, 3 H), 7.92 (d, 1 H, *J* = 8.0), 8.53 (dd, 1 H, *J* = 8.0, 2.0), 8.75 (d, 1 H, *J* = 2.0)
3h	2,4,6-$Cl_3C_6H_2$	Et	PE–Et_2O (9.8:0.2)	93	159/2.0×10^{-3}	279	98	1.29 (t, 6 H, *J* = 7.1), 3.76 (q, 4 H, *J* = 7.1),7.31 (s, 2H)
3i	2,4,6-$Br_3C_6H_2$	Et	[g]	92[h]	191/2.0×10^{-3}	411	98	1.31 (t, 6H, *J* = 7.1), 3.77 (q, 4H, *J* = 7.1),7.67 (s, 2 H)
3j	2,6-Br_2-4-FC_6H_2	Et	PE–Et_2O (9.8:0.2)	95	49.5–50.0	351	99	1.32 (t, 6 H, *J* = 7.1), 3.82 (q, 4 H, *J* = 7.1), 7.38 (d, 2 H, *J* = 8.0)
3k	2,6-Cl_2-4-$O_2NC_6H_2$	Et	PE–EtOAc (9.8:0.2)[i]	92	68.8–69.4	290	98	1.30 (t, 3 H, *J* = 7.1), 1.37 (t, 3 H, *J* = 7.1), 3.81 (q, 4 H, *J* = 7.1), 8.19 (s, 2 H)
3l	2,6-Br_2-4-$O_2NC_6H_2$	Et	C–Et_2O (9.6:0.4)	94	82.4–83.3	378	97	1.25 (t, 3 H, *J* = 7.1), 1.31 (t, 3 H, *J* = 7.1), 3.65 (q, 4 H, *J* = 7.1), 8,00 (s, 2 H)

[a] Satisfactory elemental analyses were obtained for all new triazenes 3d–l.
[b] Unless otherwise noted, yields refer to pure products isolated by column chromatography.
[c] Crystallization solvent: EtOH.
[d] PE = petroleum ether; C = cyclohexane.
[e] Lit.[17]: bp 59 °C/0.75mbar for **3a**, mp 55–56 °C for **3b** and mp 143–144 °C for **3c**.
[f] ^{1}H NMR data were identical to those reported.[17]
[g] The crude isolated product was virtually pure (TLC, ^{1}H NMR).
[h] Yield of virtually pure product (TLC, ^{1}H NMR).
[i] By flash chromatography.

tests, often with negative or misleading results, before reaching a general procedure that was completely reliable with regard to reproducibility and satisfactory yields. The difficulties we encountered could be why other authors had given up on the use of aqueous hydroiodic acid. The new procedure consists simply in adding, over a period of 30 min, the triazenes **3** dissolved in acetonitrile to a solution of aqueous hydroiodic acid in the same solvent, maintained at r.t. or heated at 60 °C and kept under vigorous stirring (Scheme 2, Procedure A). The results are reported in Table 2.

In some cases almost all the triazene had already disappeared by the end of the addition; extending the reaction time for a further 15 min brought the reactions to certain completion (entries 1, 4, 7). The triazenes **3f**, **3k** and **3l** (entries 18, 32 and 35) had significantly longer reaction times, while the triazene **3g** reaction was still incomplete even after 24 hours (entry 21). In this last case the reaction could be brought to completion by adding aqueous tetrafluoroboric acid that made the formation of the intermediate 2,4-dinitrobenzenediazonium cation easier and the overall reaction time was drastically reduced (entry 22).



Scheme 2

The addition of tetrafluoroboric acid was also useful in accelerating the reactions of **3f**, **3k** and **3l** (entries 19, 33 and 36). With regard to these particular results it must be noted, as is commonly admitted, that the conversion of 1-aryl-3,3-dialkyltriazenes in aryl iodides takes place through a two step process: first a heterolytic dissociative process that gives rise to arenediazonium cations, the second a homolytic iododediazoniation process.[10] It is quite evident that the presence of electron withdrawing groups (particularly nitro groups) on the aryl slows the first process, that gives rise to the cationic species and instead, favours the second process in that one-electron transfer involved in the iododediazoniation is facilitated. The electron donors on the aryl act in the opposite way. On the other hand it is well known that the iododediazoniation reactions have a positive outcome regardless of the nature of the substituents present on the aryl, even in the absence of a catalyst, in that the iodide ion itself is a good electron donor.[11] Therefore it was expected that the dissociative process would be the most difficult in the conversion of the 1-aryl-3,3-dialkyltriazenes **3** containing strong electron withdrawing groups, like the nitro group, to the corresponding aryl iodides. What we did find surprising was the behaviour of the triazenes **3d**, **3e**, **3h** and **3i**. In fact in these cases the iododediazoniation process did not reach completion, not even on extending the reaction times to 24 h at 60 °C, after the disappearance of the triazenes (test of azo coupling with 2-naphthol always positive; footnote h of entries 10, 14, 25 and 28). When the reactions were carried out in the presence of aqueous tetrafluoroboric acid, still at 60 °C, the process of iodededediazoniation was markedly slower than the dissociative one; nevertheless the reactions reach completion after 24 h (entries 11, 15, 26 and 29). The reaction times could be shortened, though the yields were lowered slightly, by first carrying out the dissociation of the triazenes to the corresponding diazonium cations with aqueous tetrafluoroboric acid in acetonitrile and then adding aqueous hydroiodic acid (entries 12, 16, 27 and 30). Despite the difficulties encountered, the conditions found for the conversion of the triazenes **3a**–**l** into the corresponding aryl iodides **9** are simple and efficient. The yields are certainly very good when compared with those obtained by the other known methods, considering the difficulties inherent in most of the chosen examples.

Table 2 Aryl Iodides **9**, Aryl Bromides **10** and Aryl Chlorides **11** from Triazenes **3**: Procedure A

Entry	Compd.	Ar	R	**6**	Acid	Catalyst	T[a] (°C)	Time[b] (min)	Chromatographic solvent[e]	Yield (%)[c,d]		
										Ar–I **9**	Ar–Br **10**	Ar–Cl **11**
1	**3a**	4-$MeOC_6H_4$	Me	HI			r.t.	15	PE–Et_2O (9:1)	84		
2				HBr		Cu	r.t.	15	PE–Et_2O (9:1)		81[f]	
3				HCl		Cu	r.t.	15	PE–Et_2O (9:1)			76[f]
4	**3b**	4-ClC_6H_4	Me	HI			r.t.	15	PE	71[f]		
5				HBr		Cu	r.t.	15	PE		79[f]	
6				HCl		Cu	r.t.	15	PE			68
7	**3c**	4-$O_2NC_6H_4$	Me	HI			60	15	PE–Et_2O (9:1)	88		

Table 2 Aryl Iodides **9**, Aryl Bromides **10** and Aryl Chlorides **11** from Triazenes **3**: Procedure A (continued)

Entry	Compd.	Ar	R	**6**	Acid	Catalyst	T[a] (°C)	Time[b] (min)	Chromatographic solvent[e]	Yield (%)[c,d]		
										Ar–I **9**	Ar–Br **10**	Ar–Cl **11**
8				HBr			60	15	PE–Et_2O (9:1)		83[f]	
9				HCl[g]		Cu	60	15	PE–Et_2O (9:1)			85[f]
10	**3d**	2,6-$Cl_2C_6H_3$	Et	HI			60	30[h,i]	PE	59[j] (2)		
11				HI	HBF_4 aq.		60	24 h[i,k]		83 (tr)[l]		
12				HI[m]	HBF_4 aq.		60	15		72 (tr)[l]		
13				HBr		Cu	r.t.	15	PE		70 (15)	
14	**3e**	2,6-$Br_2C_6H_3$	Et	HI			60	30[h,i]	PE	71[j] (tr)[l]		
15				HI	HBF_4 aq.		60	24 h[i,k]		79 (11)		
16				HI[m]	HBF_4 aq.		60	15		73 (3)		
17				HCl		Cu	r.t.	15	PE			79 (12)
18	**3f**	2-Cl-4-$O_2NC_6H_3$	Et	HI			60	7 h	PE–Et_2O (9.8:0.2)	74 (2)		
19				HI	HBF_4 aq.		60	30		74 (2)		
20				HBr			60	30	PE–Et_2O (9.8:0.2)		74 (9)	
21	**3g**	2,4-$(O_2N)_2C_6H_3$	Me	HI			60	24 h	PE–Et_2O (4:1)	46[n] (1)		
22				HI	HBF_4 aq.		60	4 h		82 (tr)[l]		
23				HBr			60	4 h	PE–Et_2O (4:1)		82 (tr)[l]	
24				HCl[o]	HBF_4 aq.	Cu	60	120	PE–Et_2O (4:1)			77 (5)
25	**3h**	2,4,6-$Cl_3C_6H_2$	Et	HI			60	120[h,i]	PE	54[p] (4)		
26				HI	HBF_4 aq.		60	24 h[i,k]		86 (3)		
27				HI[m]	HBF_4 aq.		60	15		75 (6)		
28	**3i**	2,4,6-$Br_3C_6H_2$	Et	HI			60	120[h,i]	PE	60 (9)		
29				HI	HBF_4 aq.		60	24 h[i,k]		84 (2)		
30				HI[m]	HBF_4 aq.		60	15		74 (13)		
31	**3j**	2,6-Br_2-4-FC_6H_2	Et	HI			60	90	PE–Et_2O (9.8:0.2)	71 (tr)[l]		

Table 2 Aryl Iodides **9**, Aryl Bromides **10** and Aryl Chlorides **11** from Triazenes **3**: Procedure A (continued)

Entry	Compd.	Ar	R	**6**	Acid	Catalyst	T[a] (°C)	Time[b] (min)	Chromatographic solvent[e]	Yield (%)[c,d]		
										Ar–I **9**	Ar–Br **10**	Ar–Cl **11**
32	**3k**	2,6-Cl_2-4-$O_2NC_6H_2$	Et	HI			60	13 h	PE–Et_2O (9.8:0.2)	65 (9)		
33				HI	HBF_4 aq.		60	60		63 (2)		
34				HBr			r.t.	3 d[q]	PE–Et_2O (9.8:0.2)		83 (tr)[l]	
35	**3l**	2,6-Br_2-4-$O_2NC_6H_2$	Et	HI			60	13 h	PE–Et_2O (9.5:0.5)	79 (7)		
36				HI	HBF_4 aq.		60	60		74 (4)		
37				HBr			60	120	PE–Et_2O (9.5:0.5)		94 (tr)[l]	
38				HCl		Cu	60	7 h	PE–Et_2O (9.8:0.2)			74 (9)
39				HCl	HBF_4 aq.	Cu	60	60				82 (3)

[a] r.t. = 20–25 °C.
[b] After the addition of triazenes **3**.
[c] Yields refer to the pure (GC, GC-MS, TLC, ^{1}H NMR) halides **9**–**11** isolated by column chromatography.
[d] Hydrodediazoniation products, that were present in all the reactions, were always isolated and in many cases also quantified; yields are reported in parentheses. In entries 1–3, 4–6 and 7–9, anisole, chlorobenzene and nitrobenzene respectively were isolated but not quantified because no particular device was adopted to avoid their loss during the workup and the following chromatography.
[e] PE = petroleum ether.
[f] Arylation products of the obtained halides were sometimes identified by GC and GC-MS analyses of the crude reaction mixtures: entries 4, 5, 8 and 9 (MS: *m/z* = 348 (M^+), 300 (M^+), 322 (M^+) and 278 (M^+), respectively). Biaryls corresponding to the intermediate diazonium salts were identified in entries 2, 3 and 5 (MS: *m/z* = 214 (M^+), 214 (M^+) and 222 (M^+), respectively).
[g] As collateral proof the reaction was carried out in the absence of Cu. After 24 h at 60 °C, 1-chloro-4-nitrobenzene was obtained in only 51% yield. By-products were nitrobenzene and 1,4-dichlorobenzene (4%).
[h] After this time a test of azo coupling with 2-naphthol was positive. It remained positive when the reaction mixture was heated at 60 °C for 24 h.
[i] The second step of iododediazoniation of the intermediate diazonium salts, i.e. 2,6-dichloro-, 2,6-dibromo-, 2,4,6-trichloro- and 2,4,6-tribromobenzenediazonium salt, formed from the corresponding triazenes **3d**, **3e**, **3h** and **3i** in the first dissociative step, was very slow in these reaction conditions. As collateral proof 2,4,6-tribromobenzenediazonium tetrafluoroborate[18] reacted at once with aq HI in acetonitrile and the corresponding iodide was obtained in 85% yield.
[j] Yield remained unvaried when the reaction was carried out at 60 °C for 24 h.
[k] A test of azo coupling with 2-naphthol was negative only after this time.
[l] tr = traces.
[m] Procedure A was modified as reported in the Experimental Section.
[n] The reaction was incomplete and **3g** was recovered in 22% yield.
[o] As collateral proof the reaction was carried out in the absence of Cu. After 24 h at 60 °C, 1-chloro-2,4-dinitrobenzene and 2,4-dinitrobenzene were obtained in 40% and 13% yield, respectively.
[p] When the reaction was carried out at 60 °C for 24 h, yield increased to 71%.
[q] At r.t. the dissociative step was very slow and after 3 days **3k** was recovered in 8% yield. The reaction was also tried at 60 °C. It was completed after 150 min. However, GC and GC-MS analyses showed the presence of the expected bromide and of a chlorosubstitution product, MS: *m/z* = 313 (M^+), in a GC ratio of 3:1.

The procedure developed for the conversion of the 1-aryl-3,3-dialkyltriazenes **3a**–**l** in aryl iodides **9** was, after appropriate adaptation, extended to the conversion of the same triazenes into the corresponding aryl bromides **10** and/or chlorides **11**. Aqueous hydroiodic acid was replaced by aqueous hydrobromic or hydrochloric acid and copper powder was added as catalyst (Table 2), except for the conversion of the triazenes **3c**,**f**,**g**,**k**,**l** into the corresponding bromides (entries 8, 20, 23, 34 and 37). These last conversions could have a positive outcome in the absence of any catalyst as the presence of nitro groups on the aryl of the triazenes **3c**,**f**,**g**,**k**,**l** allowed electron transfer to the arenediazonium cations from the bromide anion, that has, as is known,[11] a redox potential comparable to that of

iodide and chloride anions. Also the conversions of the triazenes **3a–l** into the corresponding aryl bromides **10** and/or chlorides **11** resulted in very good yields.

Various by-products were produced alongside the aryl halides **9**–**11** in the studied conversions. The main ones were the arenes (Ar-H) from the reductive dediazoniations; these were always isolated and, in many cases, also quantified. Some arylation products of the obtained halides, biaryls corresponding to the intermediate diazonium salts and various substitution products, were also present in traces and were identified by GC and GC-MS analyses of the reaction mixtures. There was never the presence of the acetanilides corresponding to the salts **1** and this testifies to the homolytic pathway of the halodediazoniation reaction.[12] No particular difficulties arose in separating the aryl halides **9**–**11** from the by-products.

Still on the theme of triazene conversion of aryl iodides, it can be observed that in one of the routes reported in the literature and cited above, the treatment with sodium iodide and a sulfonic acid cation-exchange resin in anhydrous acetonitrile was particularly efficient.[8c] Nevertheless, as the procedure requires a very expensive resin, Bio-Rad AG 50W-X12, we modified it, replacing the resin with anhydrous methanesulfonic acid (Scheme 2, Procedure B). Thus a new, convenient procedure was developed for the conversion of several of the triazenes **3a–l**, into the corresponding aryl iodides **9**. This procedure, adapted appropriately, was also successfully applied to the conversion of some triazenes into the corresponding aryl bromides **10** and chlorides **11**. The conversions were realised by reacting the triazenes **3** with methanesulfonic acid and tetraalkylammonium halides, i.e. tetrabutylammonium iodide (**7a**), tetrabutylammonium bromide (**7b**) and benzyltriethylammonium chloride (**7c**), in anhydrous acetonitrile, with or without copper as catalyst, at temperatures varying from r.t. to 80 °C (Table 3). In the case of **3g** the conversion to the corresponding iodide was incomplete, even after 24 h at 60 °C (entry 11) while that to the bromide and chloride, although requiring relatively long times, went to completion (entries 13 and 15). By replacing methanesulfonic acid with a tetrafluoroboric acid - diethyl ether complex the conversion of **3g** to **9g** and **10g** proceeded advantageously, the complex being more efficient in catalysing the dissociative process (entries 12 and 14). It should be noted however, that in the conversion of **3g** to **11g** the catalytic action of the copper was annulled by the tetrafluoroboric acid (Table 3, footnote h). Also in Procedure B, the yields of the pure aryl halides **9–11** were always good, ranging from 65% to 88%. The physical properties of all the aryl iodides, bromides and chlorides obtained according to both Procedures A and B are listed in Table 4.

In conclusion, the results of this research can be summarised as follows. In the first place we have realised a simple and efficient synthetic procedure for the preparation 1-aryl-3,3-dialkyltriazenes **3**, many of which are obtained only with difficulty by known methods; the procedure is based on the use of the dry arenediazonium *o*-benzenedisulfonimides **1**. Secondly, very high yields were achieved in the break down of the triazenes **3**, that constitute a protected form of the diazonium group, to the starting dry stable arenediazonium salts **1**. Finally, two new procedures have been developed for the conversion, in high yield, of 1-aryl-3,3-dialkyltriazenes **3** into aryl iodides **9**, bromides **10** and chlorides **11**: one is based on the use of aqueous hydrogen halides in acetonitrile, the other realised in anhydrous acetonitrile with tetraalkylammonium halides **7**, in the presence of methanesulfonic acid or, sometimes, tetrafluoroboric acid - diethyl ether complex.

Column chromatography and TLC were performed on Merck silica gel 60 (70–230 mesh ASTM) and GF 254, respectively, using the eluents reported in the Tables. Petroleum ether (PE) refers to the fraction boiling in the range 40–70 °C. Room temperature (r.t.) = 20–25 °C. ^{1}H NMR spectra were recorded on a Bruker WP80SY spectrometer. All the reagents, anhyd MeCN and the reference compounds were purchased from the Aldrich Chemical Co. Copper powder and Dowex 50X8 ion-exchange resin (H^+) were purchased from Carlo Erba and Fluka, respectively.

o-Benzenedisulfonimide (**5**) was prepared according to the literature procedure,[13] starting from *o*-benzenedisulfonyl chloride[14] and NH_3 gas, via ammonium *o*-benzenedisulfonimide and its conversion using Dowex 50X8 resin.[15]

Dry Arenediazonium *o*-Benzenedisulfonimides 1

Dry 2,6-Dibromo-4-nitrobenzenediazonium o-Benzenedisulfonimide (1l); Typical Procedure

According to the procedure previously described by us for the preparation of **1a–d**[4] and **1e,g**,[16] diazotization of 2,6-dibromo-4-nitroaniline (2.96 g, 10 mmol) was carried out with *i*-pentyl nitrite (1.29 g, 11 mmol) in the presence of *o*-benzenedisulfonimide (**5**; 2.63 g, 12 mmol) in glacial HOAc (60 mL) at 0–5 °C. A white precipitate of **1l** began to separate at once. Precipitation was completed by addition of anhyd Et_2O (100 mL). The diazonium salt was gathered by filtration on a Buchner funnel and washed several times on the funnel with anhyd Et_2O (6 × 5–6 mL) to complete the elimination of HOAc. After drying under reduced pressure, the dry titled compound **1l** was obtained in 97% yield (5.10 g). It was virtually pure (NMR, dp = decomposition point) and could be used in the next step, without further purification. For analytical purposes, a sample was purified by dissolution in hot HCOOH and precipitation with anhyd Et_2O after cooling: dp 165 °C.

^{1}H NMR (CF_3COOD): δ = 7.82 and 8.63 (2 m, 1:2).

Anal. Calcd for $C_{12}H_6Br_2N_4O_6S_2$ (526.13): C, 27.39; H, 1.15; Br, 30.37; N, 10.65; S, 12.19. Found: C, 27.40; H, 1.18; Br, 30.46; N, 10.57; S, 12.16.

Yields and physical and spectral data of the new compounds are given below.

CAUTION! In our laboratory there was no case of sudden decomposition during the preparation, purification, storage 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 manipulated carefully.

Dry 2-Chloro-4-Nitrobenzenediazonium *o*-Benzenedisulfonimide (1f)

Yield: 98%; dp 163.2–163.9 °C (HCOOH/anhyd Et_2O).

^{1}H NMR (CF_3COOD): δ = 7.52 (m, 4 H), 8.18 and 8.62 (2 d, 2 H, 1:1, J = 9.0 Hz).

Table 3 Aryl Iodides **9**, Aryl Bromides **10** and Aryl Chlorides **11** from Triazenes **3**: Procedure B.

Entry	Compd.	Ar	R	**7**	**8**	Catalyst	T[a] (°C)	Time[b] (min)	Chromatographic solvent[e]	Yield (%)[cd]		
										Ar–I **9**	Ar–Br **10**	Ar–Cl **11**
1	**3a**	4-$MeOC_6H_4$	Me	**7a**	$MeSO_3H$		r.t.	15	PE–Et_2O (9:1)	80[f]		
2				**7b**	$MeSO_3H$	Cu	r.t.	15	PE–Et_2O (9:1)		70[f]	
3				**7c**	$MeSO_3H$	Cu	r.t.	15	PE–Et_2O (9:1)			69[f]
4	**3b**	4-ClC_6H_4	Me	**7a**	$MeSO_3H$		40	15	PE	77		
5				**7b**	$MeSO_3H$	Cu	40	15	PE		82	
6				**7c**	$MeSO_3H$	Cu	40	15	PE			71
7	**3c**	4-$O_2NC_6H_4$	Me	**7a**	$MeSO_3H$		60	60	PE–Et_2O (9:1)	85		
8				**7b**	$MeSO_3H$		60	60	PE–Et_2O (9:1)		81	
9				**7c**	$MeSO_3H$	Cu	60	60	PE–Et_2O (9:1)			84
10	**3f**	2-Cl-4-$O_2NC_6H_3$	Et	**7b**	$MeSO_3H$		40	7 h	PE–Et_2O (9.8:0.2)		74 (6)	
11	**3g**	2,4-$(O_2N)_2C_6H_3$	Me	**7a**	$MeSO_3H$		60	24 h	PE–Et_2O (4:1)	35[g]		
12				**7a**	HBF_4·Et_2O		60	60		65 (15)		
13				**7b**	$MeSO_3H$		60	17 h	PE–Et_2O (4:1)		68	
14				**7b**	HBF_4·Et_2O		60	60			85 (4)	
15				**7c**	$MeSO_3H$[h]	Cu	80	16 h	PE–Et_2O (4:1)			65
16	**3i**	2,4,6-$Br_3C_6H_2$	Et	**7c**	$MeSO_3H$	Cu	40	60	PE			78 (13)
17	**3j**	2,6-Br_2-4-FC_6H_2	Et	**7a**	$MeSO_3H$		60	4 h	PE–Et_2O (9.8:0.2)	67		
18	**3l**	2,6-Br_2-4-$O_2NC_6H_2$	Et	**7b**	$MeSO_3H$		60	13 h	PE–Et_2O (9.5:0.5)		88 (2)	

[a] r.t. = 20–25 °C.
[b] After the addition of triazenes **3**.
[c] Yields refer to the pure (GC, GC-MS, TLC, ^1H NMR) halides 9–11 isolated by column chromatography.
[d] Hydrodediazoniation products, that were present in all the reactions, were sometimes isolated and quantified; yields are reported in parentheses. In entries 1–3, 4–6 and 7–9, anisole, chlorobenzene and nitrobenzene, respectively were isolated but not quantified because no particular device was adopted to avoid their loss during the workup and the following chromatography.
[e] PE = petroleum ether.
[f] Arylation products of the obtained halides were sometimes identified by GC and GC-MS analyses of the crude reaction mixtures: entries 1, 2 and 3 (MS: *m/z* = 340 (M^+), 292 (M^+), and 248 (M^+), respectively). Biaryls and diazenes corresponding to the intermediate diazonium salts were identified in entries 1–3 (MS: *m/z* = 214 (M^+) and 242 (M^+), respectively).
[g] The reaction was incomplete and **3g** was recovered in 42% yield.
[h] Using HBF_4·Et_2O at 60 °C in the presence of Cu, the reaction was complete after 30 min, but the results were unsatisfactory; in fact 1-chloro-2,4-dinitrobenzene was isolated in only 37% yield. Besides 2,4-dinitrobenzene, several unidentified by-products were present.

Anal. Calcd for $C_{12}H_7ClN_4O_6S_2$ (402.78): C, 35.78; H, 1.75; Cl, 8.80; N, 13.91; S, 15.92. Found: C, 35.74; H, 1.80; Cl, 8.83; N, 13.84; S, 15.82.

Dry 2,4,6-Trichlorobenzenediazonium *o*-Benzenedisulfonimide (1h)

Yield: 98%; dp 173.8–174.9 °C (anhyd MeCN/anhyd Et_2O).

^1H NMR (CF_3COOD): δ = 7.73 and 7.80 (2 m, 1:2).

Anal. Calcd for $C_{12}H_6Cl_3N_3O_4S_2$ (426.68): C, 33.78; H, 1.42; Cl, 24.93; N, 9.85; S, 15.03. Found: C, 33.68; H, 1.46; Cl, 24.81; N, 9.82; S, 14.95.

Table 4 Aryl Iodides **9**, Aryl Bromides **10** and Aryl Chlorides **11**: Physical Properties

Compd.	Ar	Hal	MS *m*/z (M^+)	Mp (°C) or bp (°C)/mbar[a]		Compd.	Ar	Hal	MS *m*/z (M^+)	Mp (°C)[a]	
				Found[b]	Reported[c]					Found[b]	Reported[c]
9a	4-$MeOC_6H_4$	I	234	51.0–51.5	51–52	**9f**	2-Cl-4-$O_2NC_6H_3$	I	283	99.8–100.8	100–101[19]
10a		Br	186	oil	60–61/7	**10f**		Br	235	61.0–61.5	62
11a		Cl	142	oil	71.5/9	**9g**	2,4-$(O_2N)_2C_6H_3$	I	294	86.7–87.9	87.5–88.5
9b	4-ClC_6H_4	I	238	53.3–54.1	57	**10g**		Br	246	71.6–72.9	75
10b		Br	190	65.1–65.8	67	**11g**		Cl	202	52.8–53.6	51
11b		Cl	146	53.9–55.6	54	**9h**	2,4,6-$Cl_3C_6H_2$	I	306	53.3–54.9	53–54[20]
9c	4-$O_2NC_6H_4$	I	249	173.1–174.5	174	**9i**	2,4,6-$Br_3C_6H_2$	I	438	104.–105.0	104.0–104.5[21]
10c		Br	201	125.7–127.1	127	**11i**		Cl	347	88.7–89.5	91[22]
11c		Cl	157	82.7–83.5	83	**9j**	2,6-Br_2-4-FC_6H_2	I	378	128.1–129.1	135.0–135.6[21]
9d	2,6-$Cl_2C_6H_3$	I	273	65.0–65.8	68	**9k**	2,6-Cl_2-4-$O_2NC_6H_2$	I	317	152.0–153.0	152–153[19]
10d		Br	224	64.2–64.9	65	**10k**		Br	269	87.8–88.9	88
9e	2,6-$Br_2C_6H_3$	I	360	98.5–99.5	99.0–99.5	**9l**	2,6-Br_2-4-$O_2NC_6H_2$	I	405	152.7–153.5	153.5[23]
11e		Cl	268	69.8–70.6	71	**10l**		Br	357	110.5–112.0	112
						11l		Cl	313	89.3–90.0	90–91[24]

[a] Identical physical and spectral data and retention times, by co-injection, for the resultant halides **9a–c**, **9g**; **10a–d**, **10g** and **11a–c**,**11g** and the corresponding commercially available samples of analytical purity were observed. Structures of the other halides were confirmed by comparison of their physical and spectral data with those reported in the literature.
[b] After crystallization from EtOH.
[c] Unless otherwise noted, physical data are taken from Ref.[25]

Dry 2,4,6-Tribromobenzenediazonium *o*-Benzenedisulfonimide (1i)
Yield: 99%; dp 171.5–172.1 °C (anhyd MeCN/anhyd Et_2O).

^1H NMR (CF_3COOD): δ = 7.15 and 7.93 (2 m, 2:1).

Anal. Calcd for $C_{12}H_6Br_3N_3O_4S_2$ (560.03): C, 25.74; H, 1.08; Br, 42.80; N, 7.50; S, 11.45. Found: C, 25.69; H, 1.07; Br, 42.89; N, 7.46; S, 11.51.

Dry 2,6-Dibromo-4-fluorobenzenediazonium *o*-Benzene-disulfonimide (1j)
Yield: 98%; dp 171–171.5 °C (anhyd MeCN/anhyd Et_2O).

^1H NMR (CF_3COOD): δ = 7.70 (d, 2 H, $^3J_{H-F}$ = 7.4 Hz), 7.85 (m, 4 H).

Anal. Calcd for $C_{12}H_6Br_2FN_3O_4S_2$ (499.12): C, 28.88; H, 1.21; Br, 32.02; F, 3.81; N, 8.42; S, 12.85. Found: C, 28.80; H, 1.27; Br, 31.93; N, 8.32; S, 12.77.

Dry 2,6-Dichloro-4-nitrobenzenediazonium *o*-Benzene-disulfonimide (1k)
Yield: 91%; dp 165.3 °C (anhyd MeCN/anhyd Et_2O).

^1H NMR (CF_3COOD): δ = 8.42 and 9.12 (2 m, 2:1).

Anal. Calcd for $C_{12}H_6Cl_2N_4O_6S_2$ (437.22): C, 32.96; H, 1.38; Cl, 16.22; N, 12.81; S, 14.67. Found: C, 32.93; H, 1.41; Cl, 16.15; N, 12.76; S, 14.62.

1-Aryl-3,3-dialkyltriazenes 3; General Procedure
Arenediazonium *o*-benzenedisulfonimide **1** (5 mmol) was added in small portions over a period of 5–10 min, to a vigorously stirred soln of NEt_2H (**2**, R = Et; 0.40 g, 5.5 mmol) or NMe_2H (**2**, R = Me; 40% aq soln, 7.966 M; 0.62 g, 5.5 mmol) and NaOH (0.20 g, 5 mmol) in H_2O (20 mL), maintained at 0–5 °C. Stirring was continued until completion of the reaction (30 min; absence of azo coupling with 2-naphthol). When the triazene was a solid substance, the precipitate was gathered by filtration on a Buchner funnel and then dissolved in CH_2Cl_2 (100 mL). When the triazene was an oily substance, the reaction mixture was extracted with CH_2Cl_2 (2 × 50 mL). In both the cases, the organic soln was then washed with H_2O (2 × 50 mL), dried (Na_2SO_4) and evaporated under reduced pressure. The crude residue was the title compound **3**. Some triazenes (**3d**,**e**,**g**,**i**) were virtually pure (TLC; ^1H NMR, GC-MS) and were used in the next step, without further purification. Triazenes **3a**–

c,**f**,**h**,**j–l** were purified by column chromatography. Yields reported in Table 1 refer to the pure isolated products.

The aq soln obtained after filtration or extraction of triazene **3** and the aq washings were collected and concentrated under reduced pressure to 4–5 mL and then passed through a column of Dowex 50 × 8 ion exchange resin (about 3 g for 1 g of **5**), eluting with H_2O (about 15 mL). After water removal under reduced pressure, virtually pure (^{1}H NMR) *o*-benzenedisulfonimide (**5**) was recovered in 88–99% yield: mp 192–194 °C (toluene) (Lit.[4] mp 192–194 °C).

Sometimes, the same dialkylamine **2** was used instead of sodium hydroxide. In these cases, the molar ratio **1**:**2** was 1:2.2. Triazenes **3** were obtained in comparable yields.

Chromatographic solvents, yields and physical and spectral data of triazenes **3** and yields of the recovered *o*-benzenedisulfonimide (**5**) are reported in Table 1.

Break Down of 1-Aryl-3,3-dialkyltriazenes 3 to the Starting Dry Arenediazonium *o*-Benzenedisulfonimides 1

Dry 4-Nitrobenzenediazonium *o*-Benzenedisulfonimide (1c); Typical Procedure

o-Benzenedisulfonimide (**5**; 11 mmol, 2.41 g) was dissolved in glacial HOAc (30 mL), by heating at 50–55 °C. 1-(4-Nitrophenyl)-3,3-dimethyltriazene (**3c**; 5 mmol, 0.97 g) was then added, in one portion and under stirring. A precipitate of salt **1c** began to separate at once. Heating was maintained for a further 10–15 min, until a TLC or GC control of a small portion of HOAc soln showed the disappearance of the starting triazene **3c**, previously freed from the corresponding protonated form by treatment with an aq 5% $NaHCO_3$ soln. After completion of the reaction, the mixture was cooled to about 20–25 °C, with a water bath, to complete the precipitation of the diazonium salt that was gathered by filtration on a Buchner funnel and washed several times on the funnel with anhyd Et_2O to complete the elimination of HOAc. The dry title compound **1c** was obtained virtually pure in 99% yield (1.82 g).

dp 143 °C

^{1}H NMR (CF_3COOD): δ = 7.62 (m, 4 H), 8.32 and 8.58 ppm (2 d, 4 H,1:1, *J* = 8.5 Hz).

The data were identical to those reported.[4]

The HOAc soln obtained after filtration of **1c** and the Et_2O washings were collected and concentrated under reduced pressure. The residue was virtually pure dimethylammonium *o*-benzenedisulfonimide.

^{1}H NMR (CF_3COOD): δ = 2.55 (t, 6 H, *J* = 4.5 Hz), 7.54 ppm (m, 4 H). Working as described above, the residue was passed through a column of Dowex 50X8 ion exchange resin (6 g), eluting with H_2O. After water removal under reduced pressure, virtually pure (^{1}H NMR) *o*-benzenedisulfonimide (**5**) was recovered in 99% yield (1.30 g). When the reaction mixture was cooled down to 18 °C, both **1c** and dimethylammonium *o*-benzenedisulfonimide precipitated.

According to the above procedure, also triazenes **3a**,**b**,**d–f**,**h–j** gave the corresponding diazonium salts: **1a** (1.41 g, 80%; in this case NMR spectrum of the HOAc soln obtained after filtration of the salt showed the presence of both **1a** and dimethylammonium *o*-benzenedisulfonimide, as the major products), **1b** (1.62 g, 91%), **1d** (1.76 g, 90%), **1e** (2.36 g, 98%), **1f** (1.89 g, 94%), **1h** (1.92 g, 90%), **1i** (2.58 g, 92%) and **1j** (2.25 g, 90%). For triazenes **3k**,**l** the reaction solvent was HOAc/HCOOH (30 mL, 29:1). Working as described above, **1k** and **1l** were obtained in 90% (1.97 g) and 91% (2.39 g) yield, respectively. In all the cases *o*-benzenedisulfonimide (**5**) was recovered in yield varying between 95% and 100%. The reaction failed in the case of triazene **3g**.

Aryl Halides 9–11; General Procedures

Procedure A

A soln of hydrogen halide (15 mmol), i.e. HI (57 wt.% in H_2O; 3.37 g) orHBr (48 wt.% in H_2O; 2.53 g) or HCl (35 wt.% in H_2O; 1.56 g), in MeCN (10 mL) was prepared at r.t., in the presence or absence of Cu powder (0.05 g) and maintained at r.t. or warmed at 60 °C by an oil bath (see Table 2). A soln of 1-aryl-3,3-dialkyltriazene **3** (5 mmol) in the same solvent (10 mL) was added drop wise over a period of 25–30 min, under vigorous stirring. During the addition, a slow evolution of N_2 was observed and the presence of the intermediate diazonium salt **1** was confirmed by a positive test of azo coupling with 2-naphthol. After completion of the addition, small portions of the reaction mixture were treated with an aq 5% $NaHCO_3$ soln, to free the triazene **3** that was then confirmed by TLC and GC analyses, to verify the progress of the reaction in the time. After the disappearance of **3**, stirring and heating at the indicated temperatures were maintained for a further 15 min. After this time, most of the reactions were complete (negative azo coupling test). On the contrary, the test was positive in entries 10, 14, 25 and 28. It remained still positive after 24 h at 60 °C. After completion of the reactions, GC and GC-MS analyses of the mixtures showed the aryl halides **9**–**11**, always as the major products. The hydrodediazoniation products were present in all the reactions. Among the other by-products, traces of arylation products of the obtained halides and of biaryls, corresponding to the intermediate arenediazonium salts **1**, were sometimes identified by GC-MS analysis (see footnote f of Table 2). Instead, the acetanilides corresponding to **1** were never revealed. The reaction mixtures were extracted with Et_2O (3 × 80 mL) and the combined organic extracts were washed several times with H_2O (3 × 50 mL) to eliminate all the MeCN, dried (Na_2SO_4) and evaporated under reduced pressure. The crude residues were column chromatographed to afford the pure aryl halides **9**–**11** and the hydrodediazoniation by-products.

In some reactions (Table 2: entries 19, 22, 24, 33, 36 and 39), aq HBF_4 (35 wt.% in H_2O; 25 mmol, 6.27 g) was added to the starting MeCN soln containing the hydrogen halide in the presence or absence of Cu, to make the formation of the intermediate diazonium salt easier. In particular, in the presence of aq. HBF_4 entries 11, 15, 26 and 29 came to completion after 24 h at 60 °C (negative azo coupling test).

In entries 12, 16, 27 and 30, Procedure A was modified as follows. A soln of the triazene **3d** or **3e** or **3h** or **3i** (5 mmol) in MeCN (8 mL) was added, under vigorous stirring, to a soln of aq HBF_4 (25 mmol, 6.27 g) in the same solvent (8 mL), previously heated to 60 °C. A soln of aq HI (15 mmol, 3.37 g) in MeCN (4 mL) was then added dropwise over a period of 15-20 min. After the addition was complete, a test of azo coupling with 2-naphthol was negative. The reaction mixtures were worked as described above.

Procedure B

The reactions were performed in oven-dried glassware and anhyd MeCN was used as solvent. No particular device was however adopted to exclude moisture or oxygen. A suspension of ammonium halide (12.5 mmol), i.e. tetrabutylammonium iodide (**7a**, 4.62 g), tetrabutylammonium bromide (**7b**, 4.03 g) or benzyltriethylammonium chloride (**7c**, 2.85 g), in anhyd MeCN (10 mL) was prepared at r.t., in the presence (0.05 g) or absence of Cu powder. Anhyd $MeSO_3H$ (25 mmol, 2.40 g) or $HBF_4{\cdot}Et_2O$ (54 wt.% in Et_2O; 25 mmol, 4.06 g) was added and the mixture was maintained at r.t. or warmed at a temperature varying from 40 to 80 °C (see Table 3), under vigorous stirring. A soln of 1-aryl-3,3-dialkyltriazene **3** (5 mmol) in the same anhyd solvent (10 mL) was added dropwise over a period of 25–30 min. During the addition, a slow evolution of N_2 was observed. As in Procedure A, stirring at the indicated temperature was maintained until completion of the reaction. The above work up afforded the pure aryl halides **9**–**11**.

Reaction conditions and yields of the aryl halides **9**–**11** obtained according to the above Procedures A and B are listed in Tables 2 and 3. Identical physical and spectral data and retention time, by co-injection, for the resultant pure halides and the corresponding commercially available samples of analytical purity were observed. For the halides that are not commercially available, structures and purity were confirmed by comparison of their physical and spectral data with those reported in the literature (Table 4).

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