o-Benzenedisulfonimide: an organic reagent and organocatalyst of renewed interest

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o-BENZENEDISULFONIMIDE: AN ORGANIC REAGENT AND ORGANOCATALYST OF RENEWED INTEREST

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ABSTRACT:

Synthesized nearly one century ago as a saccharine-like sweetener compound, the *o*-benzenedisulfonimide has received a discontinuous attention in the past. In the last century, various synthetic procedures have been reported, in confirmation of the interest in this intriguing compound. In recent years, it has been used as a leaving group in reactions of nucleophilic substitution of amines with alcohols or phenols to give the corresponding ethers. Its *N*-fluoroderivative is a stable and efficient fluorinating agent, which has found applications in several asymmetric syntheses. In previous studies, its conjugated base has been extensively used as stabilizing counter-ion of arenediazonium salts; safely isolated and stored in a dry state, ready to use, they have been applied successfully in many dediazoniation reactions, with interesting mechanistic insights. More recently, due to its high acidity, the *o*-benzenedisulfonimide has been used in catalytic amounts in some common acid-catalyzed organic reactions. Valuable aspects of this catalyst are its easy recovery from the reaction mixture and its reuse in other reactions, with clear economic and ecological advantages. Finally, the disulfonimide functional group has been proposed as a powerful chiral motif for strong Brønsted acids in asymmetric organocatalysis.

Keywords: *o*-benzenedisulfonimide, organic synthesis, stabilizing anion, organocatalysis, recoverable catalyst, recyclable catalyst**.**

In this review, we report a survey of the literature concerning the synthetic applications and the useful potential of an organic reagent and organocatalyst of renewed interest, the *o*-benzenedisulfonimide (**1**), and its derivatives.

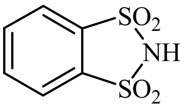

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Fig. (1).

Cyclic disulfonimides are strong Brønsted acids: their acidity is comparable to that of strong mineral acids, higher than acyclic analogues; the acid-strengthening effect of the sulfonyl groups is likely enhanced by the incorporation in the five-membered ring [1a]. Several such compounds are reported in literature: by varying the ring size from 4 to 9, a substructure search on CAS databases resulted in 495 substances (using SciFinder software client, updated on 06/29/2009), most of them perfluorinated. In this review, we will cover the literature concerning synthesis, reactivity, and applications of the title compound and derivatives, following the chronological development.

1. SYNTHESIS OF *o*-BENZENEDISULFONIMIDE AND DERIVATIVES

1.1 SYNTHESIS OF *o*-BENZENEDISULFONIMIDE (1) AND RELATED STRUCTURES

In general, cyclic disulfonimides have been prepared either by cyclization of disulfonyl halides (chlorides or fluorides) with ammonia and subsequent *N*-derivatization, or by cyclization of disulfonyl chlorides with ammonia derivatives. As a consequence, the key intermediate for the synthesis of the 1,3,2-benzodithiazole-1,1,3,3-tetraoxide (*o*-benzenedisulfonimide, **1**) is the *o*-benzenedisulfonyl chloride (**2**). This, by reaction with ammonia or derivatives, gives always the imide derivatives as major products, along with very low amounts of the corresponding bisamides.

All syntheses of **1** differ only by the starting reagent to prepare **2**, the intermediate reaction steps or the purification procedure. The only real difference in the cyclization of *o*-benzenedisulfonyl chloride is that with nitrous acid, followed by reduction of the intermediate *N*-hydroxy derivative.

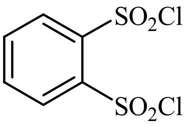

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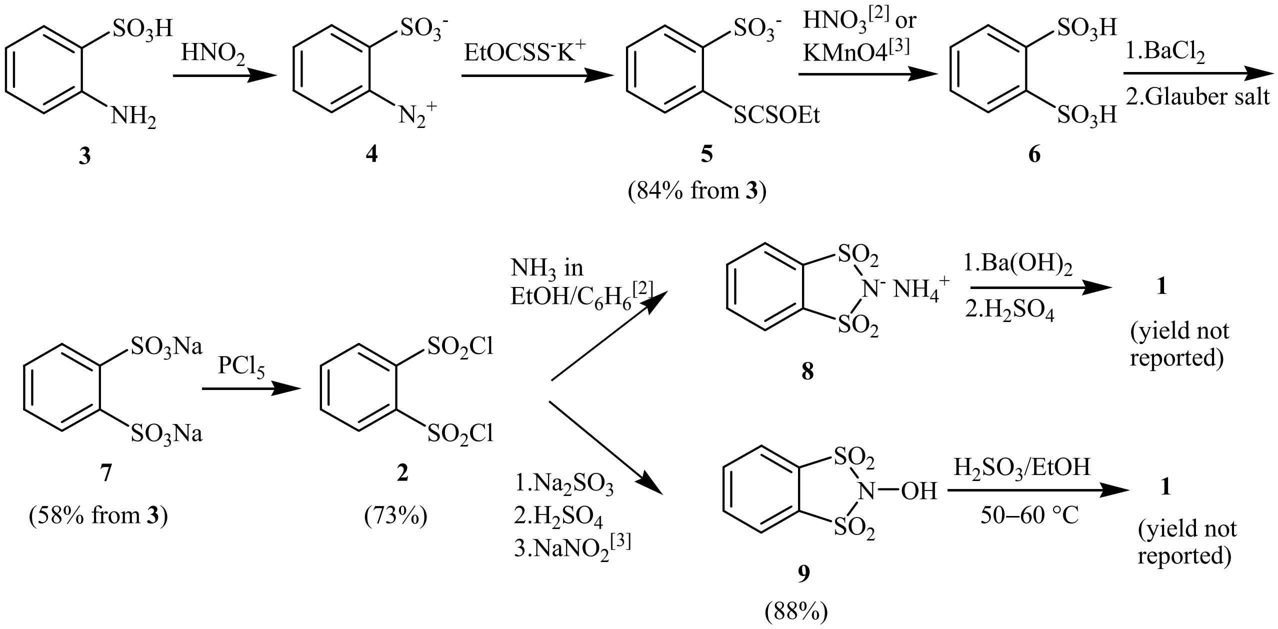
Fig. (2).

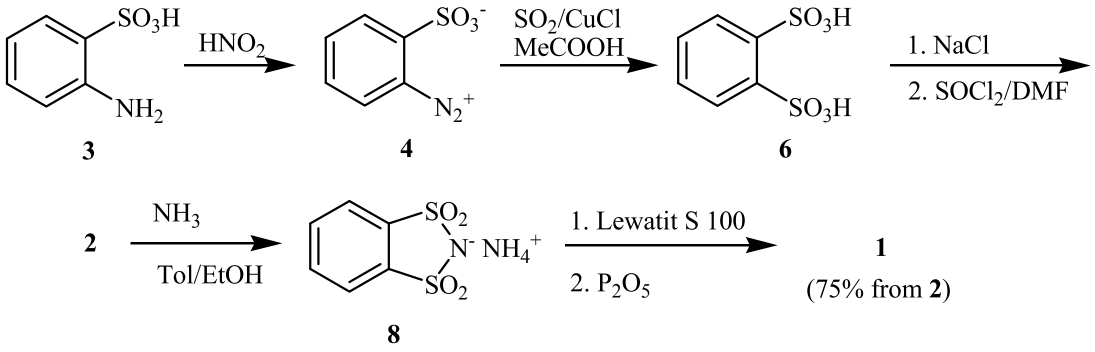
o-Benzenedisulfonimide was synthesized for the first time by Holleman [2] and Hurtley and Smiles [3], nearly contemporarily, in 1921 and 1926. Both syntheses started from *o*-aminobenzenesulfonic acid (**3**) via a very troublesome multistage route, and were differing in the oxidation step (HNO$_3$ or KMnO$_4$) and in the conversion of the disulfonyl chloride **2** into disulfonimide **1,** via acidification of the intermediate ammonium salt **8** [2] or via reduction of the *N*-hydroxy derivative **9** (Scheme 1) [3].



Scheme 1.

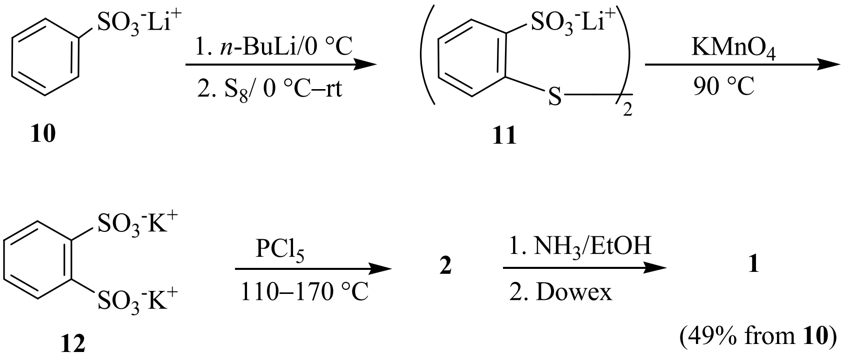
These procedures were successively modified by Hendrickson and co-workers [4], by using gaseous ammonia in benzene/ethanol for the cyclization step (quantitative yield of ammonium salt, “sweet taste”), and Dowex 50X8 ion-exchange resin for the purification of **1** (79% yield from **2**).

They described the acid **1** as “fully ionized in (and not extractable from) water and ... possess acidity comparable to that of hydrochloric acid”. In 1993 Blaschette’s group [5] modified substantially the preparation of the disulfonyl chloride **2** from acid **3** [6], using then gaseous ammonia in toluene/ethanol for the cyclization step and Lewatit S 100 ion-exchange resin for the purification (Scheme 2).



Scheme 2.

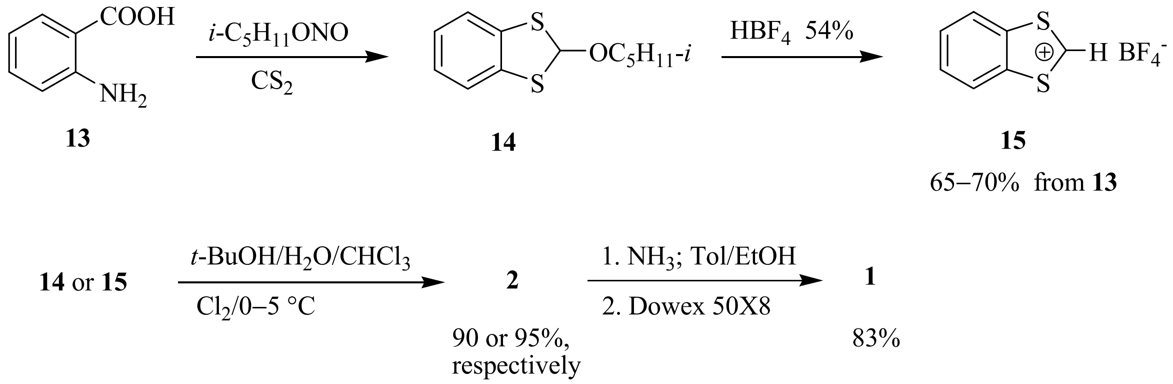
An improved synthesis of *o*-benzenedisulfonimide was proposed by Davis and co-workers [7], in a four-step process starting from Li-benzenesulfonate (**10**) (49% overall yield); the sole purification step was the final filtration on Dowex ion-exchange resin (Scheme 3).



Scheme 3.

Finally, two procedures have been reported to prepare the disulfonyl chloride **2**. In 1986, it was prepared starting from anthranilic acid (**13**), through its conversion into the intermediates 2-(3-methylbutoxy)-1,3-benzodithiole (**14**) or 1,3-benzodithiolium tetrafluoroborate (**15**), and treatment with chlorine/water; the overall yield of **2** from **13** was 46% via isolated **14** or 62–67% via isolated

15 [8]. The product **2** was then converted into **1** in 83% yield by a slightly modified procedure (Scheme 4) [9].



Scheme 4.

The second procedure was patented in 1996: amongst a number of aromatic and heteroaromatic sulfonyl halides prepared by oxidative chlorination or bromination of methyl sulfides or methyl sulfoxides, in the presence of water, **2** was obtained in 82% yield from *o*-bis(methylsulfanyl)benzene (**16**) [10].

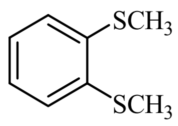


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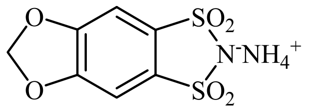
Fig. (3).

In conclusion, the key intermediate of the above syntheses is *o*-benzenedisulfonyl chloride (**2**), which accordingly can now be prepared starting from the commercially available *o*-benzenedisulfonic acid dipotassium salt [3,7], anthranilic acid [8], *o*-aminobenzenesulfonic acid [2–4,6,11], and from *o*-bis(methylsulfanyl)benzene [10]. In recent times, *o*-benzenedisulfonyl chloride has become commercially available, and now also *o*-benzenedisulfonimide is sold.

Structurally related to *o*-benzenedisulfonimide are compounds **17** [12], **18** [13], and **19** [14]; **17** and **18** were obtained from the corresponding disulfonyl chlorides and ammonia, and **19** by pyrolysis of the corresponding N-R derivatives (N-R derivatives were prepared from the disulfonic anhydride and primary amines, then treated with P_2O_5; direct reaction with ammonia failed). No further studies were done after their synthesis.



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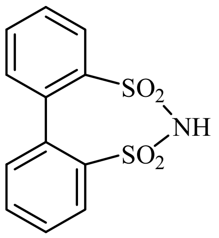

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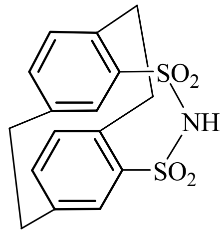

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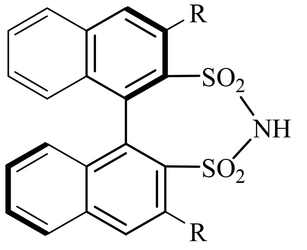
Fig. (4).

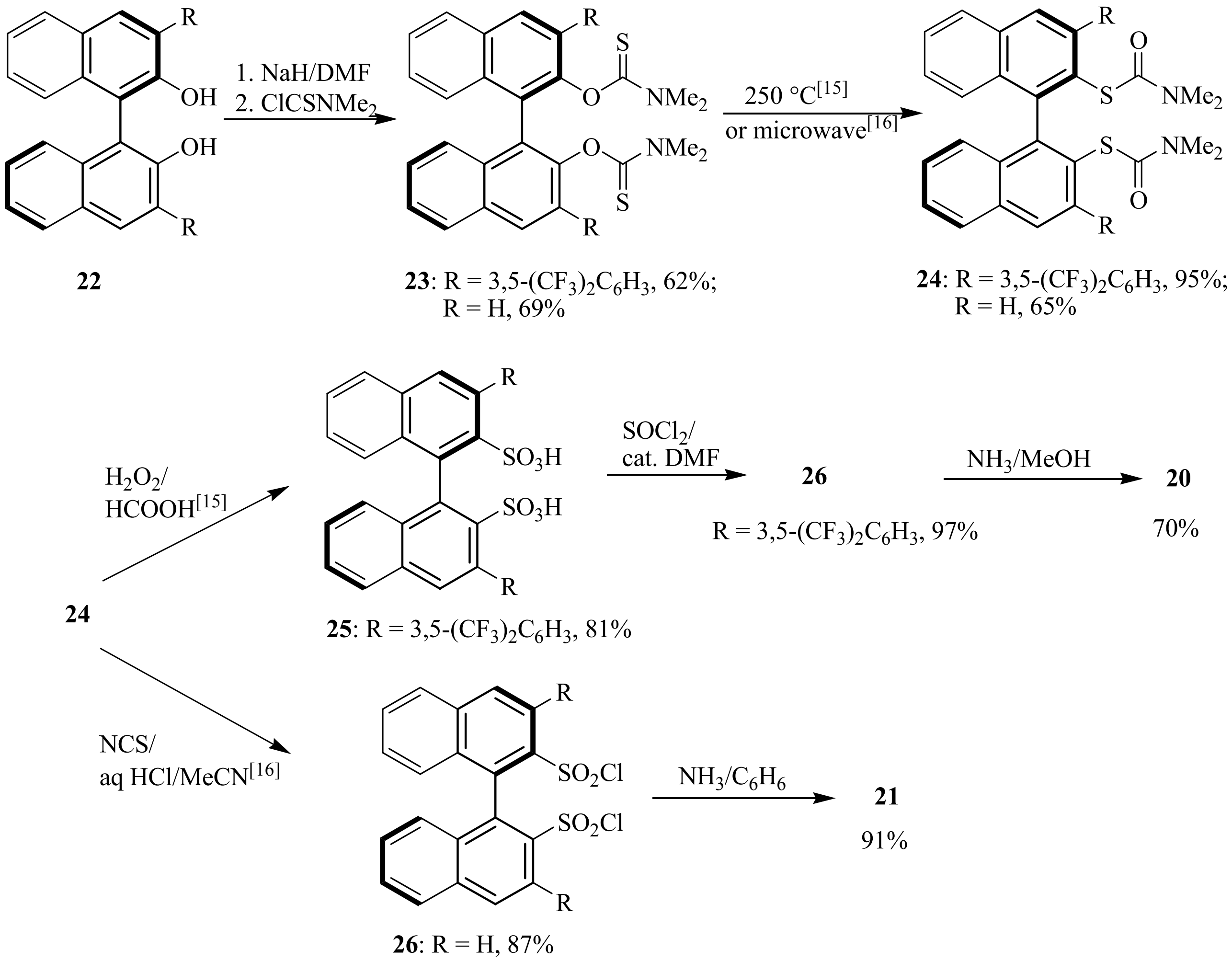
In confirming the renewed interest in this class of compounds, while this manuscript was being reviewed, two studies regarding the cyclic disulfonimides **20** [15] and **21** [16] below have been published. The disulfonimide functional group has been introduced as new chiral motif in these strong Brønsted acids.



20; R = 3,5-$(CF_3)_2C_6H_3$
21; R = H

Fig. (5).

(*R*)-3,3’-Bis[3,5-bis(trifluoromethyl)phenyl]-1,1’-binaphthyl-2,2’-disulfonimide (**20**) and (*R*)-1,1’-binaphthyl-2,2’-disulfonimide (**21**) were synthesized from the optically pure 1,1’-binaphthyl-2,2’-diols **22** through the intermediate *O*,*O*’-diaryl bis(N,N-dimethylthiocarbamates) **23**, then isomerized to the *S*,*S*’-diaryl bis(N,N-dimethylthiocarbamates) **24** by a Newman–Kwart rearrangement. The two synthetic procedures differ on the subsequent oxidation step and conversion to the disulfonyl chlorides **26**, key intermediates of the target chiral imides (Scheme 5).

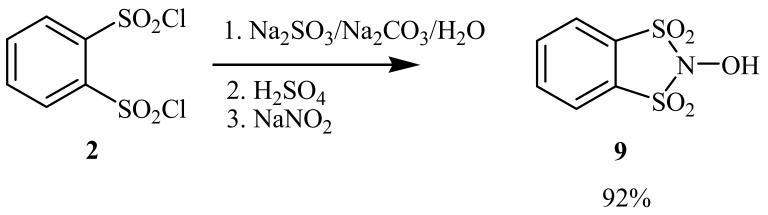


Scheme 5.

1.2 SYNTHESIS OF *o*-BENZENEDISULFONIMIDE DERIVATIVES

N-Hydroxy-*o*-benzenedisulfonimide (9):

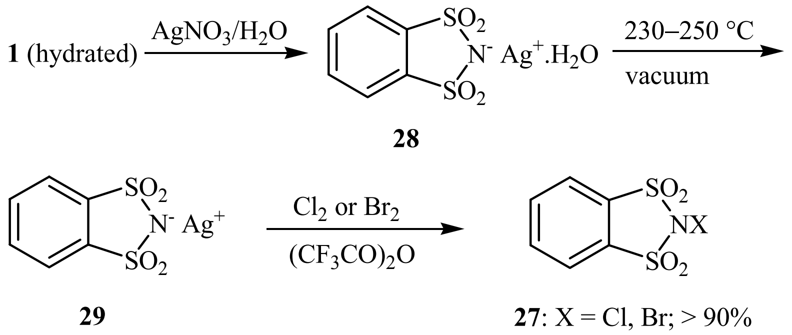
N-Hydroxy-*o*-benzenedisulfonimide (**9**) was first prepared by Hurtley and Smiles in 88% yield through reduction of *o*-benzenedisulfonyl chloride (**2**) and then reaction with nitrous acid (Scheme 1) [3]. The same sequence was adopted by Hendrickson and co-workers giving 83% yield of **9** [4], and then improved by Kice and Liao in 1981 (92% yield of product) (Scheme 6) [17].



Scheme 6.

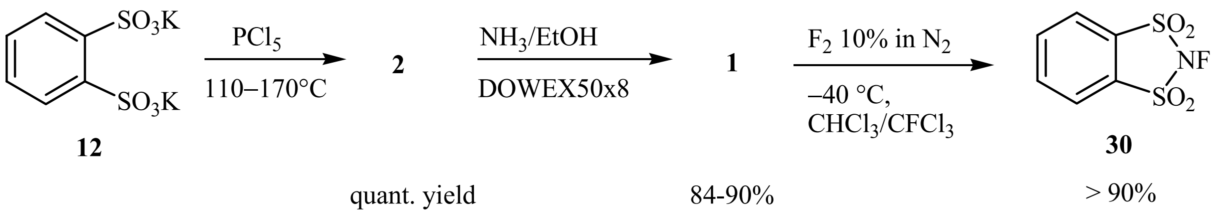
N-Halogen-*o*-benzenedisulfonimides (27, 30):

In Hendrickson's fundamental work, several derivatives of *o*-benzenedisulfonimide were prepared as attractive synthetic tools, since the imide anion seemed to be a good leaving group, owing to the charge stabilization by the two sulfonyl moieties. Unfortunately, most of these compounds did not show the expected reactivity; only halides **27** (X = Cl, Br) were very active sources of halogen cations. Their synthesis was achieved by treating anhydrous silver *o*-benzenedisulfonimide **29** (from **1** and silver oxide) with chlorine or bromine in trifluoroacetic anhydride (Scheme 7) [4].



Scheme 7.

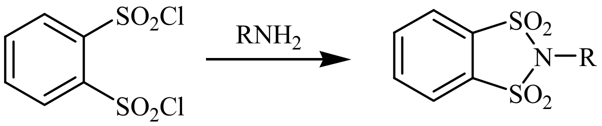
N-Fluoro-*o*-benzenedisulfonimide **30** was synthesized in high yield by Davis and co-workers about 30 years later, as a stable and easily prepared highly efficient source of "electrophilic" fluorine, and until now it has been used in a significant number of reactions (Scheme 8) [18].



Scheme 8.

N-Aryl, *N*-Alkyl and *N*-dialkylaminoalkyl-*o*-benzenedisulfonimides (31):

N-Aryl and *N*-arylalkyl *o*-benzenedisulfonimide **31** were prepared according to Hurtley and Smiles [3] from *o*-benzenedisulfonyl chloride and aniline in essentially quantitative yield, or with primary arylalkyl amines in EtOH solution, in the presence of sodium acetate: in this case the bisamides were recovered in considerable amounts (Scheme 9) [4].

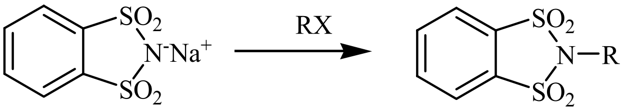


2 **31**

R = Ph (quant.), $PhCH_2$ (36%), $PhCH_2CH_2$ (51%)

Scheme 9.

N-Alkyl analogues **31** were unusually prepared in low yields by electrophilic alkylation, by refluxing sodium *o*-benzenedisulfonimide (**32**) with alkyl iodides or dialkylaminoalkyl chlorides in ethyleneglycol monoethyl ether-water mixtures (Scheme 10) [19].



32 **31**

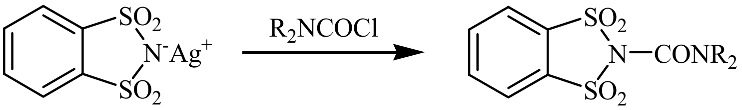
R = Me (37%); Et (56%); Pr (34%); Bu (57%);
$Et_2NCH_2CH_2$ (55%); $Et_2NCH_2CH_2$ CH_2 26%);
$Bu_2NCH_2CH_2$ (62%)

Scheme 10.

N-Methyl analogue (**31**; R = Me) was also prepared in quantitative yield from anhydrous silver *o*-benzenedisulfonimide (**29**) and methyl iodide in acetonitrile [20], whilst *N*-1-adamanthyl analogue was prepared from **29** and 1-bromoadamanthane in anhydrous benzene in 95% yield [21]. Poor yields of *N*-phenyl-*o*-benzenedisulfonimide were obtained in transamidation reaction of sulfonimide **1** and aniline at 184–200 °C, whilst good yields were obtained starting from *N*-methyl-*o*-benzenedisulfonimide [22].

N-Dialkylcarbamoyl-*o*-benzenedisulfonimides (32):

Title compounds **32** were prepared treating silver *o*-benzenedisulfonimide (**29**) with diethyl or dimethylcarbamoyl chloride (Scheme 11) [23]; the molecular crystal structure was determined, the urea moiety showed a non-planar geometry.

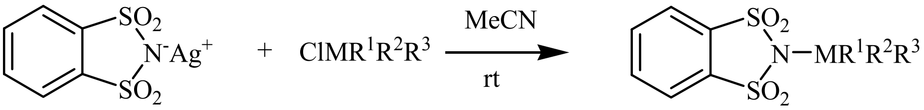


29 **32**

Scheme 11.

N-Trialkylsilyl and *N*-trialkylstannyl-*o*-benzenedisulfonimides (33) (34) :

Prepared by metathesis of silver 1,2-benzenedisulfonimide (**29**) with the appropriate trialkyl chlorosilane or chlorostannane, their crystal structures were determined [24]. Compounds **33** displayed unusually long bonds between the trigonal-planar *N* and the tetrahedrally coordinate Si atom [24b]; the solid state structures suggested that the N-Si bond lengthening in these disulfonylated aminosilanes is induced by the π-acceptor character of the sulfonyl groups.



29

33: M = Si
34: M = Sn

Scheme 12.

Miscellaneous *N*-derivatives:

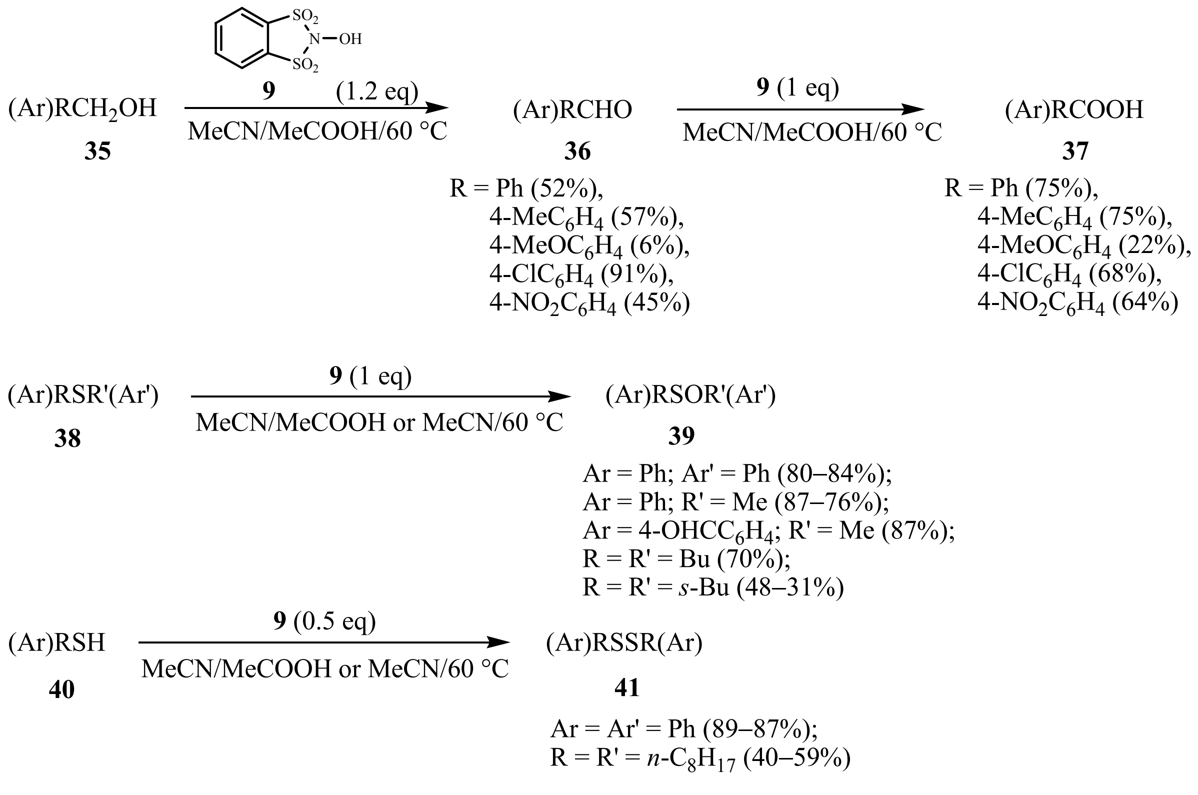
In order to check the activity of the conjugate base as good leaving group in electrophilic substitution reactions, several *N*-substituted derivatives were synthesized [4]. With the exception of the more promising compounds cited above (**9**,**27**,**30**), *N*-methoxy-*o*-benzenedisulfonimide was prepared by reaction with diazomethane but without synthetic developments, whilst other derivatives could not be prepared.

2. SYNTHETIC APPLICATIONS OF *o*-BENZENEDISULFONIMIDE AND DERIVATIVES

2.1 *o*-BENZENEDISULFONIMIDE DERIVATIVES

***N*-Hydroxy-*o*-benzenedisulfonimide (9):**

Compound **9** was studied as a potential source of hydroxyl cations (as a peracid) both as Baeyer-Villiger reagent and oxidant agent of aldehydes to acids, but the results were negative [4]. Nearly 30 years later, the oxidizing properties of **9** were reconsidered and exploited by Degani and Fochi in the conversions of benzyl alcohols **35** to benzaldehydes **36**, benzaldehydes **36** to benzoic acids **37**, sulfides **38** to sulfoxides **39**, and thiols **40** to disulfides **41** (Scheme 13) [25]. The reaction conditions were mild, highly selective regarding the oxidation of sulfides to sulfoxides, and chemoselective: 4-(methylsulfanyl)benzaldehyde gave excellent yield of the corresponding sulfoxide, leaving the formyl group unchanged.



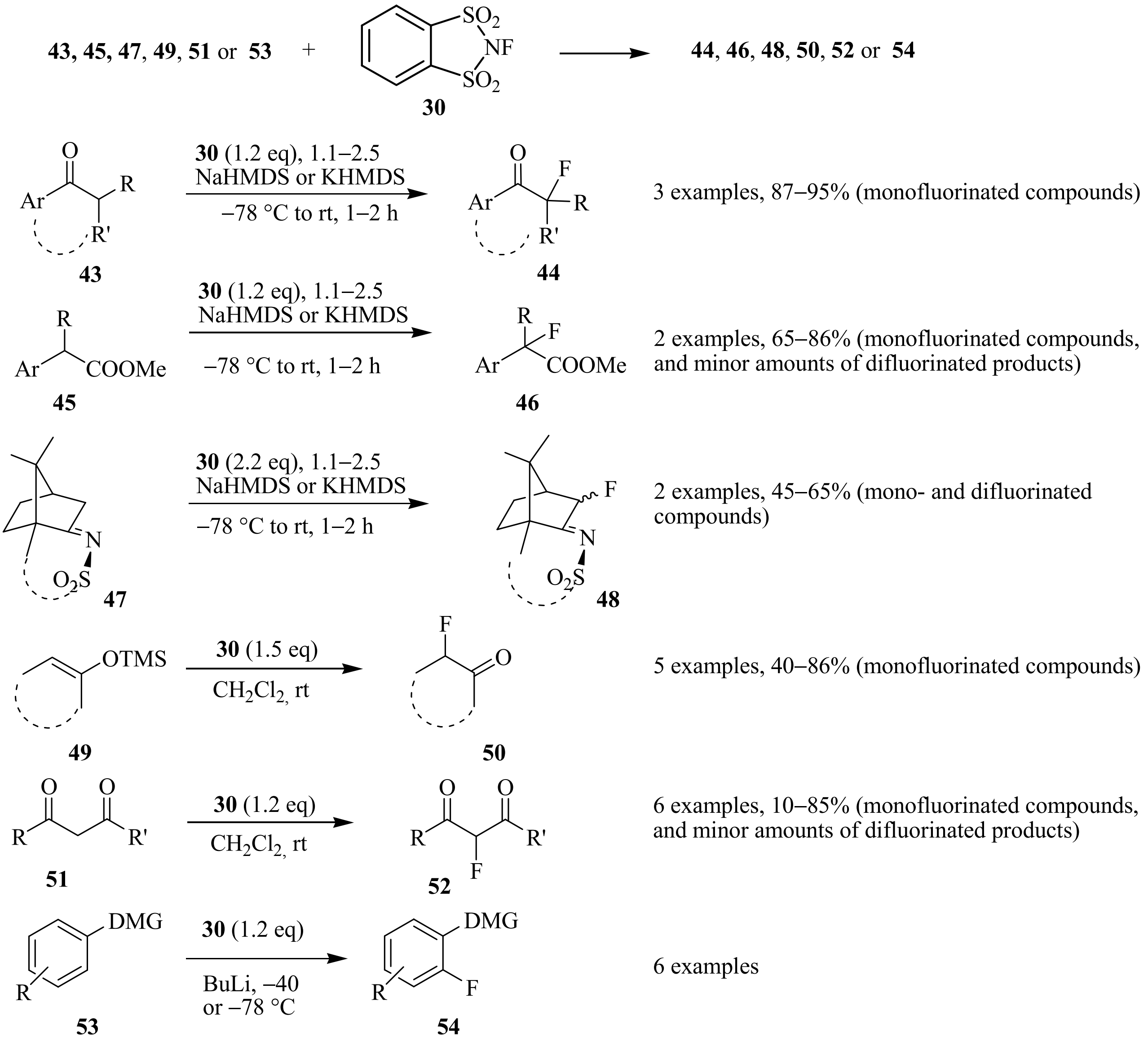
Scheme 13.

N-Fluoro-*o*-benzenedisulfonimide (30):

Although inactivated aromatic compounds were efficiently halogenated by using *N*-chloro- and *N*-bromo-*o*-benzenedisulfonimide (**27**) [4], these reagents did not receive further studies. Only *N*-fluoro analogue is currently used as a halogenating agent.

As confirmed by the number of scientific publications, electrophilic fluorination has recently attracted considerable attention in organic synthesis, since fluorinated chemicals find applications in organic, agricultural, medicinal and material chemistry fields. Furthermore, several examples of asymmetric synthesis of fluorinated molecules have been successfully achieved. The topic is covered in many reports, and synthetic applications of compound **30** have been reviewed and compared with other fluorinating agents [26]. Without discussing all the examples, we will report on the most significant ones below.

N-Fluoro-*o*-benzenedisulfonimide (NFOBS, **30**) was synthesized as above by Davis and co-workers (Scheme 8); they also performed the most significant work in the area of electrophilic fluorination of metal enolates (enolates, azaenolates, 1,3-dicarbonyl compounds, *ortho*-methalated aromatic compounds, silyl enol ethers [18b]), and highly diastereoselective electrophilic fluorination of chiral metal enolates (imide enolates [27]). *N*-Fluoro reagents with different reactivities have been developed to overcome the limitations of fluorinating procedures employing highly reactive, corrosive and toxic reagents. Amongst them, *N*-fluoro-*o*-benzenedisulfonimide (**30**) and *N*-fluorobenzenesulfonimide [$(PhSO_2)_2NF$, NFSI, **42**] are particularly interesting because of their high reactivity, stability and ease of preparation. In the cited paper [18b], metal enolates, silyl enol ethers, and 1,3-dicarbonyl compounds gave α-fluorinated products in high yields. Good control of monofluorination *versus* difluorination was generally observed. Interestingly, difluorination was explained by the enolization, and hence the difluorination, induced by the acidity of the *o*-benzenedisulfonimide. NFOBS was sufficiently reactive to directly fluorinate activated aromatics, but not selectively. Regiospecific reaction was accomplished on aromatic organometallic compounds: Grignard reagent, phenyllithium, and *ortho*-lithiated aromatic substrates (generated from directed metalation group aromatics, DMG, with alkyllithiums). Both **30** and **42** showed similar reactivity, but better yields were obtained with **30** in metal enolates, Grignard reagents and lithium reagents fluorination, whereas **42** gave better yields in the fluorination of lithiated arenes (Scheme 14). The difference has been related to the cyclic structure of **30** that makes the approach of the nucleophile more favourable for steric reasons and makes **1** a leaving group better than the acyclic benzenesulfonimide; the mechanism suggested is a S_N2-type.



3 examples, 87–95% (monofluorinated compounds)

2 examples, 65–86% (monofluorinated compounds, and minor amounts of difluorinated products)

2 examples, 45–65% (mono- and difluorinated compounds)

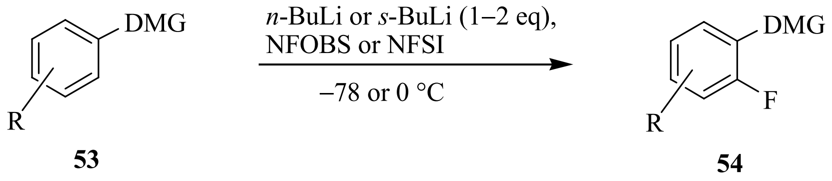
5 examples, 40–86% (monofluorinated compounds)

6 examples, 10–85% (monofluorinated compounds, and minor amounts of difluorinated products)

6 examples

Scheme 14.

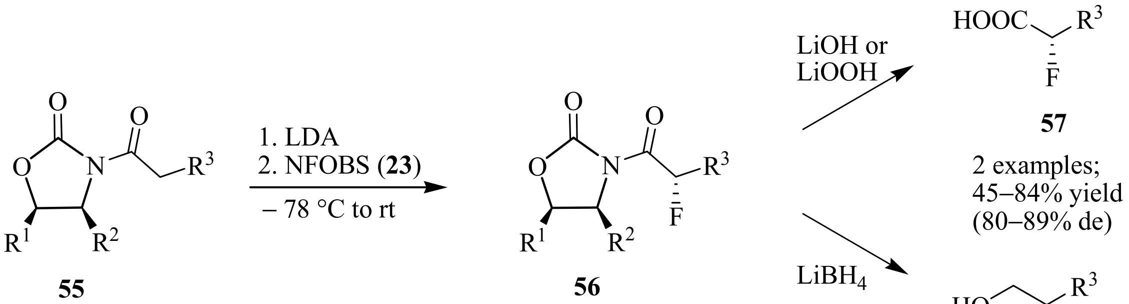
Several examples of regiospecific synthesis of fluorinated aromatics using NFOBS and/or NFSI in the presence of DMG have also been reported [28] (Scheme 15).



DMG = CONHBu, OCSNEt$_2$, SO-*t*-Bu, SO$_2$NHMe,
SO$_2$NMe$_2$, SO$_2$NEt$_2$, SO-*t*-Bu, SO$_2$-*t*-Bu

Scheme 15.

In the diastereoselective fluorination of chiral imide enolates, Davis and co-workers used Evans' oxazolidinones (**55)** [29] as chiral auxiliaries to prepare the α-fluoroacids **57** and the β-fluoroalcohols **58** with good *de*. Due to the enhanced acidity of the α-fluoro proton, some racemization occurred during the removal of the chiral auxiliary under basic conditions, whilst this was avoided by reducing with LiBH$_4$. The efficiency of NFOBS (**30**, Scheme 16) [29] was compared with that of NFSI (**42**) [30] as fluorinating agent: compound **30** was proved to approach from the less hindered *si*-face of the imide enolate.



2 examples;
45–84% yield
(80–89% de)

56: R^1 = Ph, R^2 = Me, R^3 = *n*-Bu 88% yield (97% de)
R^1 = H, R^2 = *i*-Pr, R^3 = *n*-Bu 85% yield (96% de)
R^1 = Ph, R^2 = Me, R^3 = *t*-Bu 86% yield (96% de)
R^1 = H, R^2 = *i*-Pr, R^3 = *t*-Bu 80% yield (97% de)
R^1 = Ph, R^2 = Me, R^3 = PhCH$_2$ 84% yield (89% de)
R^1 = Ph, R^2 = Me, R^3 = Ph 86% yield (86% de)

58

5 examples;
45–84% yield
(89–95% de)

Scheme 16.

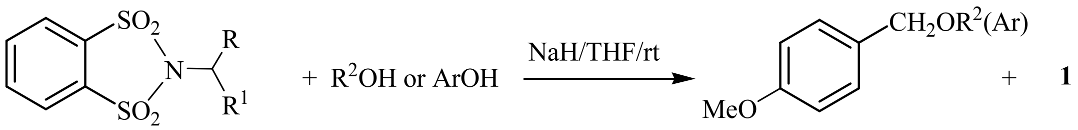
In one case, NFSI showed a better diastereoselectivity because of its greater steric bulk [31]. The procedure for asymmetric synthesis of fluoroorganic compounds has been applied to obtain 2-deoxy-2-fluoropentoses as final products from a non-carbohydrate precursor, and a fluorinated analogue of the side chain of the taxol [32].

N-Aryl, *N*-alkyl and *N*-dialkylaminoalkyl-*o*-benzenedisulfonimides (31):

Prepared in 1969 by Hendrickson [4] in order to study the feasibility of the C-N bond cleavage, these compounds appeared surprisingly inert, even by treatment with sodium cyanide or base or during sublimation at elevated temperatures: so the idea that *o*-benzenedisulfonimide anion would be a facile and useful leaving group was abandoned.

As in the case of compound **9**, thirty years later, these products and naphthalene analogues received attention again. These derivatives were synthesized from the corresponding disulfonyl chlorides and primary amines (as major products along with traces of bisamides [34,35) by Carlsen and Fiksdahl, in the course of a wider study on nucleophilic substitution reactions of *N*,*N*-disulfonylimides; they were usefully converted with good stereoselective control of the reactions.

These imides were then used in benzylation of alcohols or phenols (Scheme 17) [33], in stereoselective nucleophilic substitution of the starting chiral amines [34,35], and finally in stereoselective synthesis of optically active aryl alkyl ethers from enantiopure amines or alcohols [36].



24

R = 4-$MeOC_6H_4$; R^1 = H

59

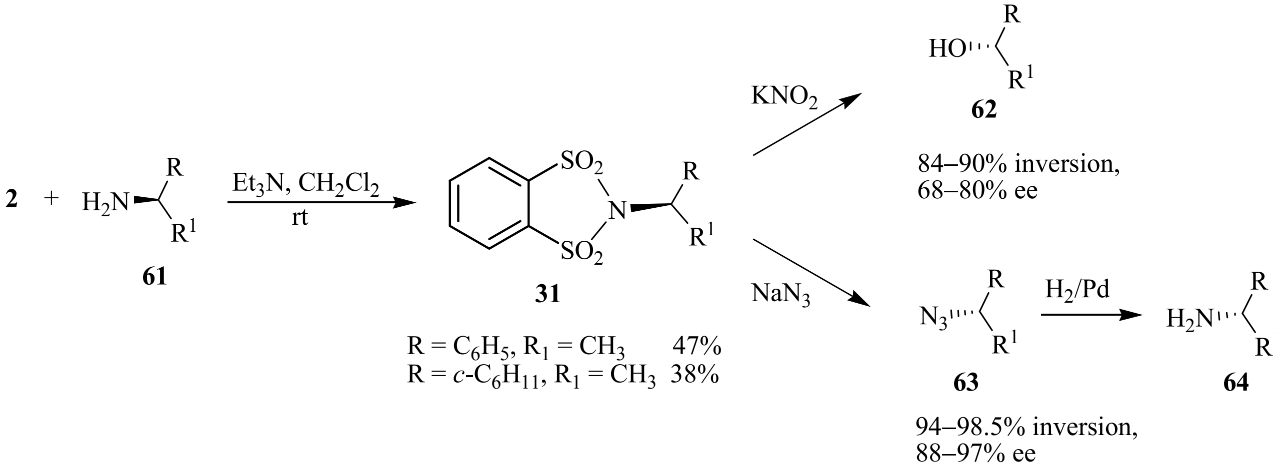
3 examples; 57–78%

Scheme 17.

Treatment of *N*-(4-methoxybenzyl)-1,2-benzenedisulfonimide with aqueous KOH in DMF yielded 4-methoxybenzyl alcohol, confirming that these reactions represented a mild procedure for the conversion of amines into the corresponding alcohols [33].

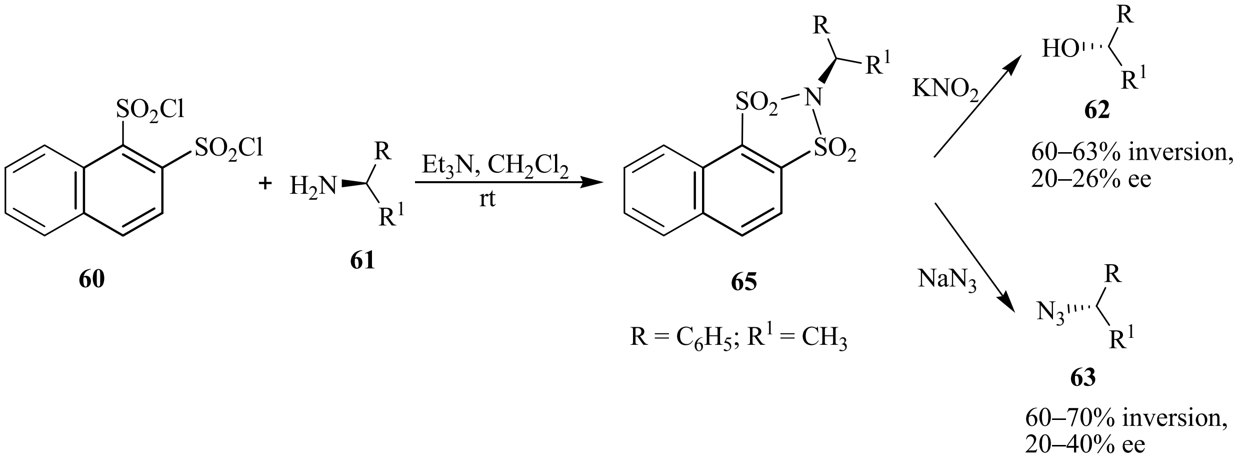
o-Benzenedisulfonyl chloride **2** or 1,2-naphthalenedisulfonyl chloride **60** and enantiopure primary amines **61** were reacted in dichloromethane in the presence of Et_3N (Schemes 18 and 19) [33,34,35].

The enantiomerically pure derivatives **31** were easily converted into alcohols **62** or azides **63** by nucleophilic attack of KNO_2 and NaN_3 respectively, with inversion of configuration at the chiral centre; reduction of the azido group afforded the inverted amines **64** (Scheme 18). The nucleophilic substitution was easier on the benzylic substrate; higher stereoselectivity was obtained carrying out the reactions in DMSO (84–90 and 94–98.5% inversion for **62** and **63**, respectively) and by decreasing the reaction temperature, as expected for a S_N2 mechanism.



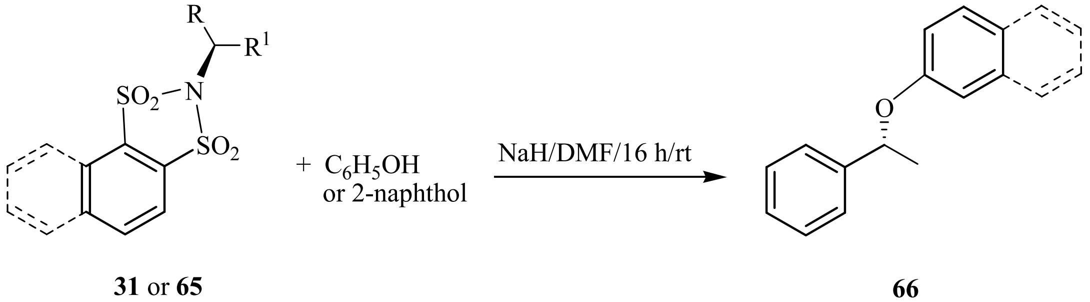
Scheme 18.

The above conversions were then applied to the naphthalene derivatives **65**; however in this case the observed stereoselectivity was lower (Scheme 19). The result was explained by a higher contribution from an ionic or ion pair mechanism, owing to a greater stability of the naphthalene leaving group relative to the benzene, and not to a better nucleophilicity of the former anion compared to the latter [35].



Scheme 19.

The same authors studied the stereoselective synthesis of chiral aryl ethers from an enantiopure amine, through the *o*-benzene- or the 1,2-naphthalenedisulfonimide intermediates (Scheme 20). The 1-phenylethyl phenyl (or 2-naphthyl) ethers **66** were formed in 39–44% (or 57–68%) yields and 83–87% (or 70–79%) inversion [36]. Alternative methods of preparation of **66** via benzyne or TFA ester showed higher selectivity.



R = C_6H_5; R^1 = CH_3

Scheme 20.

2.2 *o*-BENZENEDISULFONIMIDE as STABILIZING COUNTER-ION of DRY ARENEDIAZONIUM SALTS

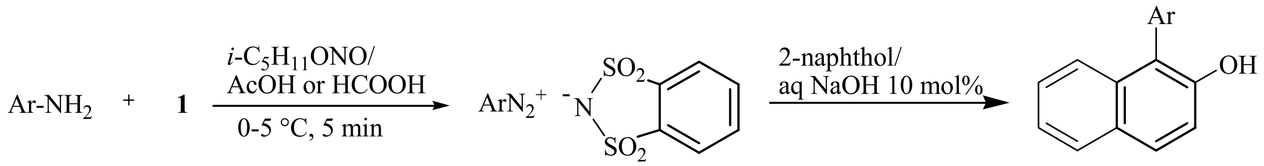
It is well-known that arenediazonium salts are quite unstable in the dry state, potentially explosive [37], but arenediazonium tetrafluoroborates, sulfonates, trifluoroacetates, nitrates or salts with complex anions have been proposed as exceptions to this behaviour.

Bearing in mind two brief notes described some arenediazonium salts stabilized by fluorinated disulfonimides [38], Degani first thought about the advantage of utilizing the anion of *o*-benzenedisulfonimide as stabilizing counter-ion of arenediazonium cations, even in the dry state, and then to revisit some synthetic applications of this versatile class of compounds. This resulted, in the last decade, in a significant number of papers by Degani's research group.

Other studies were focused on selected arenediazonium *o*-benzenedisulfonimides, whose kinetics and azocoupling reactions were investigated for comparison with related tetrafluoroborates, confirming similar reactivity of both classes of diazonium salts, but greater stability and easier experimental procedures for dry salts **67** [39].

Dry arenediazonium *o*-benzenedisulfonimides (67):

Dry arenediazonium *o*-benzenedisulfonimides **67** were easily prepared by diazotization of aromatic amines **68** with isopentyl nitrite in the presence of **1** (1.2 equiv) in glacial acetic acid or in formic acid at 0–5 °C. The dry salts were always obtained in excellent yields and high purity, as proved by the conversion into the corresponding (2-hydroxy-1-naphthyl)aryldiazenes **69** (Scheme 21). The ionic nature of salts **67** was confirmed by the X-ray analysis of one of these salts [9,40]. They are soluble in water as well as in polar protic and aprotic solvents, but insoluble in apolar or slightly polar solvents, exceptionally stable, storable for long periods, and ready to be used.



68 **67** **69**

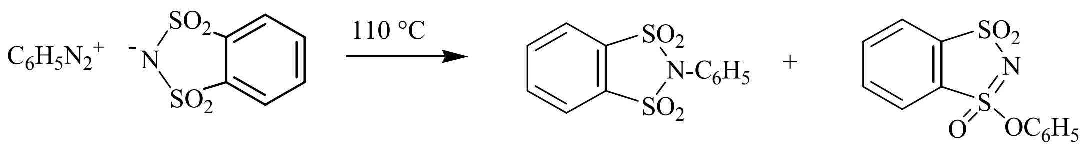
Ar = Ph; 2-, 3-, 4-MeC$_6$H$_4$;
2-, 3-, 4-MeOC$_6$H$_4$; 2-, 3-, 4-ClC$_6$H$_4$;
2-, 3-, 4-BrC$_6$H$_4$; 2-, 3-, 4-NO$_2$C$_6$H$_4$;
4-Me$_2$NC$_6$H$_4$; 2,6-Me$_2$C$_6$H$_3$;
2,6-Cl$_2$C$_6$H$_3$; 1-naphthyl

20 examples; 85–99%

20 examples; 84–99%

Scheme 21.

Since they have high, well-defined and reproducible decomposition points, decomposition of benzenediazonium *o*-benzenedisulfonimide (**70**, dp 110 °C) was studied in the presence and in the absence of toluene. In both cases, two products **71** and **72** were isolated, the former being predominant (**71** : **72** = 79 : 14 or 66 : 18, respectively) (Scheme 22). The reaction carried out in solvent furnished also a mixture of three isomers of phenylation of toluene, with an isomeric ratio consistent with a heterolytic mechanism. This clue and the poor electron donor properties of the *o*-benzenedisulfonimide anion induced the authors to suggest a heterolytic decomposition mechanism.



70 **71** **72**

Scheme 22.

Salts **67** have been successfully converted in several classes of compounds; dediazoniation reactions with *O*, *S*, *N*, and *C* nucleophiles, in aqueous or organic medium, gave isolated yields of pure products comparable or often higher than those reported with conventional methods. It has to be highlighted that a further valuable aspect of all procedures reported below is the easy recovery of *o*-benzenedisulfonimide (**1**). After workup of the reaction mixtures, **1** was recovered in good to high yield and so reusable for the preparation of other arenediazonium salts, with noticeable economic and ecological advantages.

For general literature references dealing with each dediazoniation reaction, we refer to the literature cited in each article.

Diaryldiazenes and aryl(*tert*-butyl)diazenes (73):

The first synthetic application of salts **67** was the synthesis of diaryldiazenes and aryl(*tert*-butyl)diazenes **73** by electrophilic *C*-coupling reactions of these salts with Grignard reagents (**74**) in equimolar amounts. The procedure was of general validity and gave high yields of products. In all the reactions, two isomeric products were observed, but complete isomerization of the *Z* into the *E* isomer was achieved by heating at 70 °C (Scheme 23) [41].

$$\mathbf{67} + \underset{\mathbf{74}}{\mathrm{(Ar')RMgX}} \xrightarrow{\mathrm{THF},\ -78\ ^{\circ}\mathrm{C}} \underset{\mathbf{73}}{\mathrm{ArN{=}NR(Ar')}}$$

21 examples; 61–91%
3 examples; 45–52%

Ar = Ph; 2-, 4-ClC_6H_4; 3-,4-$MeOC_6H_4$; 3-,4-BrC_6H_4
Ar' = Ph; 4-MeC_6H_4; 4-ClC_6H_4
R = *t*-Bu

Scheme 23.

Aryl methanesulfonates (75):

Aryl methanesulfonates **75** (and three aryl trifluoromethanesulfonates) were easily prepared by thermal decomposition of some representative salts **67** in methanesulfonic acid (or trifluoromethanesulfonic acid), at a temperature between 60 and 120 °C, in reproducible good yields (Scheme 24) [42]. The authors suggested that the reaction follows a D_N+A_N mechanism (Nucleofuge Detachment + Nucleophile Attachment) of dediazoniation. The failure of the reaction with *ortho* substituted arenediazonium salts and the decomposition reaction of benzenediazonium *o*-benzenedisulfonimide (**70**) in methanesulfonic acid in the presence of toluene or nitrobenzene confirmed the suggested mechanism. Small amounts of substituted biphenyls were detected and the ratio of the isomeric products was consistent with an electrophilic phenylation.

$$\mathbf{67} + CH_3SO_3H \xrightarrow{60\text{–}120\ °C} \underset{\mathbf{75}}{ArOSO_2CH_3} \qquad \text{15 examples; 70–90\%}$$

Ar = Ph; 2-, 3-, 4-MeC_6H_4;
2-, 3- ,4-$MeOC_6H_4$; 2-, 3-, 4-ClC_6H_4;
2-, 3-, 4-BrC_6H_4; 2-, 3-, 4-$NO_2C_6H_4$;
2-$MeSC_6H_4$; 2-FC_6H_4;
2-, 3-$CF_3C_6H_4$; 1-naphthyl

Scheme 24.

Aryl chlorides, bromides, and iodides (76):

Halodediazoniation reactions of a wide range of dry arenediazonium *o*-benzenedisulfonimides **67** by using tetraalkylammonium halides **77** (2.5 equiv) were carried out in anhydrous acetonitrile at room temperature in the presence of copper catalyst, or at 60 °C (or room temperature) without catalyst. In 60 examples, yields were 61–94%, only in few cases were lower (8 examples, yields 51–55%) (Scheme 25) [43].

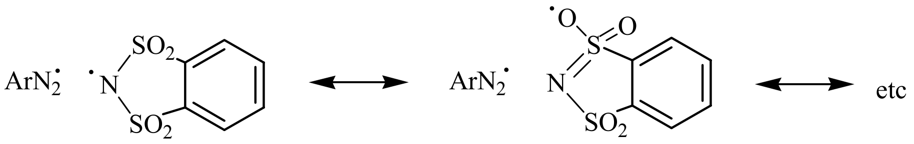
$$\mathbf{67} + \underset{\mathbf{77}}{Q^+X^-} \xrightarrow[\text{(Cu)}]{\text{rt or 60 °C}} \underset{\mathbf{76}}{Ar\text{-}X} \qquad \begin{array}{l}\text{60 examples; 61–94\%}\\ \text{8 examples; 51–55\%}\end{array}$$

Q^+X^- = $Bu_4N^+I^-$, $Bu_4N^+Br^-$,
$Et_3PhCH_2N^+Cl^-$

Ar = Ph; 2-, 3-, 4-MeC_6H_4;
2-, 3-, 4-$MeOC_6H_4$; 2-, 3-, 4-ClC_6H_4;
2-, 3-, 4-BrC_6H_4; 2-, 3-, 4-$NO_2C_6H_4$;
2-$PhSO_2C_6H_4$;
2,4-$(NO_2)_2C_6H_3$; 1-naphthyl

Scheme 25.

Normally halodediazoniation reactions follow a homolytic pathway: chloro and bromodediazoniation are catalyzed by metal ions or metals (acting as electron transfer agents to arenediazonium ions), whilst in the iodidodediazoniation the iodide directly transfers one electron to the cation. Nevertheless, by using arenediazonium *o*-benzenedisulfonimide, at 60 °C in the absence of copper, all aryl bromides were obtained in slightly lower yields than those in the presence of catalyst (and at room temperature); on the contrary, only arenediazonium salts bearing strong electron-withdrawing groups in *ortho* and/or *para* positions on the aromatic ring, gave chlorodediazoniation products without catalyst at 60 °C. The explanation provided by the authors was that the anion of salt **67** could act as a primary electron donor reagent, giving rise to the outer-sphere (or not bonded) electron transfer complex **78**. This would then easily react with the bromide, but not with the chloride (except for the above substituted salts), according to the redox potentials of the two halide anions.

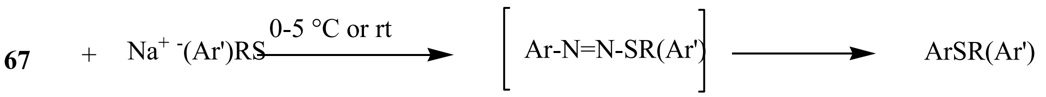


78

Fig. (6).

Alkyl aryl and diaryl sulfides (79):

It is well-known that alkyl and arylthiodediazoniation are dangerous reactions, due to the formation and accumulation of the highly explosive intermediate diazosulfides **81**. By using arenediazonium *o*-benzenedisulfonimides **67,** the reactions of Stadler and Ziegler were slightly modified and transformed into an efficient and safe procedure, of general applicability [44]. Various unfunctionalized and functionalized alkyl aryl and diaryl sulphides (**79**) were prepared by reacting dry salts **67** with sodium thiolates **80** (1.1 equiv) in anhydrous methanol, at 0–5 °C for the alkylthiodediazoniation and room temperature for the arylthiodediazoniation (Scheme 26).



$$67 + Na^+ \, {}^-(Ar')RS \xrightarrow{0\text{-}5\ °C \text{ or rt}} [Ar\text{-}N{=}N\text{-}SR(Ar')] \longrightarrow ArSR(Ar')$$

80 **81** **79**: 63 examples

Ar = Ph; 2-, 3-, 4-MeC_6H_4; 2-, 3-, 4-$MeOC_6H_4$; 2-, 3-, 4-ClC_6H_4; 2-, 3-, 4-BrC_6H_4; 2-, 3-, 4-$NO_2C_6H_4$; 4-CNC_6H_4; 4-$HOOCC_6H_4$; 2-, 4-HOC_6H_4; 4-$MeOOCC_6H_4$; 2-$MeSC_6H_4$; 2,4-$(NO_2)_2C_6H_3$; 2,6-$Cl_2C_6H_3$; 1-naphthyl
Ar' = Ph; 2,6-$Me_2C_6H_3$; 2,6-$Cl_2C_6H_3$; 2,6-$Br_2C_6H_3$
R = Me, Bu, *s*-Bu, *t*-Bu, *c*-C_6H_{11}, *n*-C_6H_{13}, *n*-C_8H_{17}, *n*-$C_{16}H_{33}$, CH_2Ph, CH_2COOH, CH_2CH_2COOH, CH_2CH_2OH

Scheme 26.

In 63 examples, the yields were generally high; lower yields were obtained from sterically hindered arenediazonium cations or thiols. The mechanism of these reactions proceeds through a homolytic pathway, as confirmed by the observed negligibility of the substituent electronic effects and also by a radical diagnostic test. Nonetheless, the authors proposed a $S_{RN}2$ mechanism, alternative to the $S_{RN}1$ suggested for arylthiodediazoniation of arenediazonium tetrafluoroborates [45]. A bimolecular $S_{RN}2$ homolytic chain process would better account for the reported observations and results: rate reaction increased by protic solvent, nearly equimolar amounts of reactants, considerable amounts of disulfides and arenes as by-products in the arylthiodediazoniation, halogen substitution never observed in halogen-substituted arenediazonium salts, and strong steric effects of bulky substituents on the *ortho* positions of either reactants.

Aryl thiocyanates (83):

Aryl thiocyanates are generally prepared by thiocyanodediazoniation of diazotized aromatic amines and metal thiocyanates in aqueous solutions, mostly under Sandmeyer-type reaction conditions. However, this synthetic route suffers some limitations, such as low yields, considerable by-product formation, nucleophilic substitution of other aromatic ring substituents. All these drawbacks were overcome by using arenediazonium *o*-benzenedisulfonimides. Several aryl thiocyanates (**83**) were prepared in high yields and purity by reaction of dry **67** and sodium thiocyanate (1.1 equiv, in almost cases; **82**) in anhydrous acetonitrile at room temperature in the presence of copper powder or at 50 °C (or room temperature) in the absence of catalyst (Scheme 27) [46].

$$\underset{}{\mathbf{67}} + \underset{\mathbf{82}}{\mathrm{Na^{+}SCN^{-}}} \xrightarrow[\text{(Cu)}]{\text{rt or 50 °C}} \underset{\mathbf{83}\text{: 22 examples; 30–100\%}}{\mathrm{ArSCN}}$$

Ar = Ph; 2-, 3-, 4-MeC_6H_4; 2-, 3-, 4-$MeOC_6H_4$; 2-, 4-ClC_6H_4;
4-IC_6H_4; 2-, 3-, 4-$NO_2C_6H_4$; 2-, 4-$MeOOCC_6H_4$;
4-CNC_6H_4; 2,6-$Me_2C_6H_3$; 2,4-$(NO_2)_2C_6H_3$;
2,6-$Br_2C_6H_3$; 2,5-$Cl_2C_6H_3$; 2-$PhSO_2C_6H_4$

Scheme 27.

As already reported for bromodediazoniation [43], the thiocyanodediazoniation is a homolytic process, also in the absence of copper: the anion of the *o*-benzenedisulfonimide behaves as an electron transfer reagent, giving rise to the electron transfer complex previously hypothesized. These considerations were supported by diagnostic tests and comparative reactions with arenediazonium tetrafluoroborates.

1-Aryl-3,3-dialkyltriazenes (85) and conversion in aryl halides (76):

Triazenes are a biologically interesting and synthetically useful class of compounds. Normally they are prepared by reaction of arenediazonium salts with secondary or cyclic amines, but there are several cases where their synthesis is particularly troublesome. Several 1-aryl-3,3-dialkyltriazenes **85** were prepared in high yields by reaction of dry salts **67** (also deriving from weakly basic aromatic amines) with dimethyl or diethylamine (1.1 equiv; **84**) and NaOH (1 equiv), or with above amines (2.2 equiv) in aqueous solution at 0–5 °C (Scheme 28) [47].

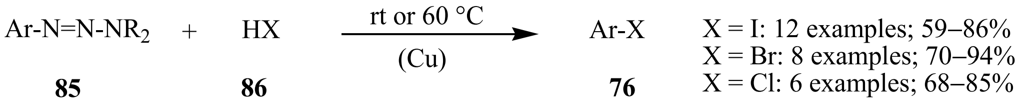
$$\underset{}{\mathbf{67}} + \underset{\mathbf{84}}{\mathrm{R_2NH}} \xrightarrow[\mathrm{H_2O\ (NaOH)}]{\text{0–5 °C}} \underset{\mathbf{85}\text{: 12 examples; 90–95\%}}{\mathrm{Ar{-}N{=}N{-}NR_2}}$$

Ar = 4-$MeOC_6H_4$; 4-ClC_6H_4; 4-$NO_2C_6H_4$; 2,6-$Br_2C_6H_3$; 2,6-$Cl_2C_6H_3$; 2,4-$(NO_2)_2C_6H_3$;
2,4,6-$Cl_3C_6H_2$; 2,4,6-$Br_3C_6H_2$; 2-Cl-4-$NO_2C_6H_3$; 2,6-Cl_2-4-$NO_2C_6H_2$; 2,6-Br_2-4-$NO_2C_6H_2$;
R = Me, Et

Scheme 28.

It is known the ability of triazenes to break down to release *in situ* diazonium ions, that directly reacted; the deprotection of the diazonium group is normally affected by acid and this can be a problem for the *in situ* subsequent reactions. The authors performed this break down by heating triazenes with *o*-benzenedisulfonimide (2.2 equiv, **1**) in acetic acid or acetic acid-formic acid mixture: the dry salts **67** were separated from the dialkyl ammonium salt by cooling the reaction mixture at room temperature. This procedure is potentially very useful in organic synthesis, as it allows chemical modifications of both the intermediate triazene and the reconstituted arenediazonium salt.

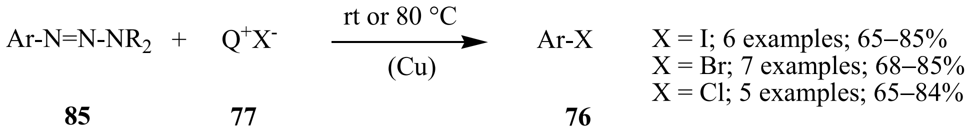
Furthermore, aryltriazenes **85** were converted into corresponding aryl iodides, bromides and chlorides **76**, following two alternative procedures. The former used simply aqueous hydrogen halides **86** (3 equiv) in acetonitrile at room temperature or 60 °C, sometimes in the presence of aqueous HBF_4 or copper powder (Scheme 29).



Scheme 29.

The presence of HBF_4 was necessary for iodo and chlorodediazoniation of arenediazonium salts bearing strong electron-withdrawing substituents on the aromatic ring. The reason was that, in these cases, the triazene heterolytic dissociation, first step of the reaction, was slowed down, whilst the successive homolytic iododediazoniation was favoured. Finally, copper powder was needed in the conversion of the triazenes **85** into aryl chlorides and bromides, except for bromides from triazene nitro substituted: in these cases, the substituent enabled the electron transfer to the arenediazonium group from the bromide anion.

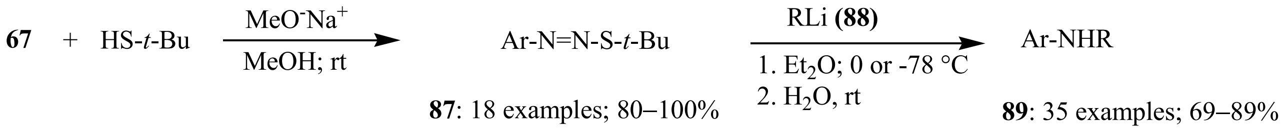
The second procedure used anhydrous methanesulfonic acid and tetraalkylammonium halides **77** in anhydrous acetonitrile at temperatures ranging from room temperature to 80 °C, sometimes in the presence of copper powder, as mentioned above (Scheme 30).



Scheme 30.

N-Alkylanilines (89):

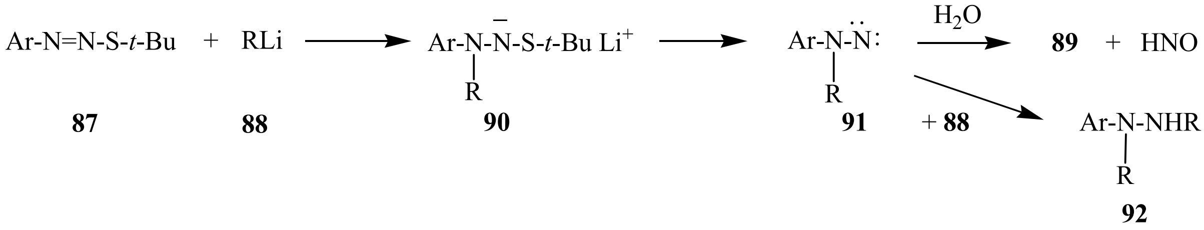
N-Monoalkylanilines **89** were selectively prepared from arenediazonium salts **67** with alkyllithiums (2.2 equiv; **88**) [48], through synthesis and isolation of the corresponding intermediate (*Z*)-(*tert*-butylsulfanyl)(aryl)diazenes **87** [44]. (Alkylsulfanyl or arylsulfanyl)(aryl) diazenes are highly unstable, decomposing *in situ* into the corresponding sulphides; exceptions are diazenes **87**, that behave as a protected form of the diazonium functional group, like the better known triazenes. Unexpectedly, treatment of **87** with an alkyllithium in anhydrous diethyl ether at 0 °C or at –78 °C led selectively to pure *N*-monoalkylation products (Scheme 31).



Ar = Ph; 2-, 4-MeC_6H_4; 4-$MeOC_6H_4$; 2-FC_6H_4; 2-ClC_6H_4; 2-, 3-, 4-BrC_6H_4; 2-$MeSC_6H_4$; 4-CNC_6H_4; 2,6-$Me_2C_6H_3$; 2,6-$F_2C_6H_3$; 2,6-$Cl_2C_6H_3$; 2,6-$Br_2C_6H_3$; X-$C_6H_4CH_2C_6H_4$
R = Me, Bu, *s*-Bu, *n*-C_6H_{13}

Scheme 31.

Besides the synthetic usefulness of the reaction, the authors proposed an interesting mechanism, on the basis of constant traces of hydrazines **92** as by-products and of suitable collateral proofs. Whilst the evidence of the intermediate **90** is almost certain, greater caution must be taken for the nitrene **91**. It is worthwhile to highlight the umpolung of the amino nitrogen atom, in the diazene protected form, reacting as an electrophile towards carbanions (Scheme 32).



Scheme 32.

S-Aryl thiol esters (95):

An easy and safe procedure for the synthesis of *S*-aryl thiol esters **95** has been set up starting from arenediazonium *o*-benzenedisulfonimides **67** with sodium thioacetate or thiobenzoate (**93**) (2 equiv) in dry acetonitrile; the intermediate diazo thiol esters **94** were observed (Scheme 33) [49]. In all the considered examples, the yields were higher than those reported in literature, regardless of nature and position of the substituents on the aromatic ring.

$$\mathbf{67} \quad + \quad \underset{\mathbf{93}:\ R = CH_3,\ C_6H_5}{Na^{+}\,{}^{-}SCOR} \longrightarrow \underset{\mathbf{94}}{\left[\text{Ar-N=N-S-COR}\right]} \longrightarrow \underset{\mathbf{95}}{\text{Ar-S-COR}}$$

28 examples; 81–100%

Scheme 33.

Hydrodediazoniation with hydrogen peroxide:

A wide range of variously substituted dry salts **67** were hydrodediazoniated by hydrogen peroxide (30 wt% in H_2O; 2 equiv, **96**), in THF at reflux, yielding pure arenes **97** in high yields, in the presence of both electron-donating or electron-withdrawing substituents, and also of steric hindrance (Scheme 34). Collateral proofs in the presence of radical reaction inhibitors, or aryl radical trapping agents, led the authors to hypothesize a free radical mechanism [50].

$$\mathbf{67} \; + \; \underset{\mathbf{96}}{H_2O_2} \xrightarrow[\text{reflux}]{\text{THF}} \text{Ar-H}$$

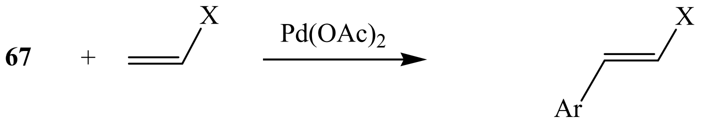
97: 18 examples; 68–100%

Ar = 4-MeC_6H_4; 4-BuC_6H_4; 2-PhC_6H_4; 4-$MeOC_6H_4$; 4-$PhOC_6H_4$; 2-$MeSC_6H_4$; 4-$NO_2C_6H_4$; 4-$MeCOC_6H_4$; 4-CNC_6H_4; 2,6-$Me_2C_6H_3$; 2,6-$Br_2C_6H_3$; 2,4,6-$Me_3C_6H_2$; 2,4,6-$Br_3C_6H_2$; 2-Me-5-$NO_2C_6H_3$; 3,5-$(MeO)_2C_6H_3$

Scheme 34.

Heck-type arylation reactions:

Finally, the synthetic usefulness of dry arenediazonium *o*-benzenedisulfonimides **67** was tested in transition metal catalyzed cross-coupling reactions. They were first studied as electrophiles in Heck-type arylation reactions, arenediazonium salts (mainly tetrafluoroborates) being a valid alternative to conventional aryl halides and triflates [51]. Some common olefinic substrates used in this reaction were arylated by a wide range of arenediazonium salts **67** in the presence of $Pd(OAc)_2$ (1 mol% with respect to **67**), in a suitable organic solvent. No ligands were necessary, complete stereoselectivity was observed and yields were excellent, regardless of the nature of the substituents (this finding being in contrast with the difficulties reported in literature for nitro substituted arenediazonium tetrafluoroborates [52]). Ethyl acrylate (**98**, 1.2 equiv), acrylic acid (**99**, 1.5 equiv), acroleyne (**100**, 1.5 equiv), and styrene (**101**, 1.2 equiv) gave high yields of arylated products **102**–**105**, always in (*E*)-configuration; in the case of **99** and **100**, a base (anhydrous $CaCO_3$, in equimolar amount to **99** or **100**) and anhydrous conditions were needed (Scheme 35).



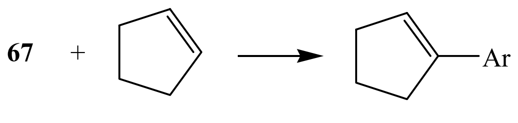
98, X = COOEt
99, X = COOH
100, X = CHO
101, X = Ph

102, X = COOEt; 15 examples, 42–100%
103, X = COOH; 4 examples, 55–96%
104, X = CHO; 5 examples 83–95%
105, X = Ph; 3 examples, 54–83%

Ar = 2-, 4-MeC_6H_4; 2-, 3-, 4-$MeOC_6H_4$; 4-ClC_6H_4; 3-, 4-BrC_6H_4; 4-IC_6H_4; 2-, 4-$NO_2C_6H_4$; 2-$HOOCC_6H_4$; 2,4-$(NO_2)_2C_6H_3$; 2-MeOCO-3-thienyl

Scheme 35.

Heck-type arylation of cyclopentene (**106**, 1.2 equiv) gave 1-arylderivatives **107**, with greater selectivity compared to corresponding reactions of tetrafluoroborates (Scheme 36).



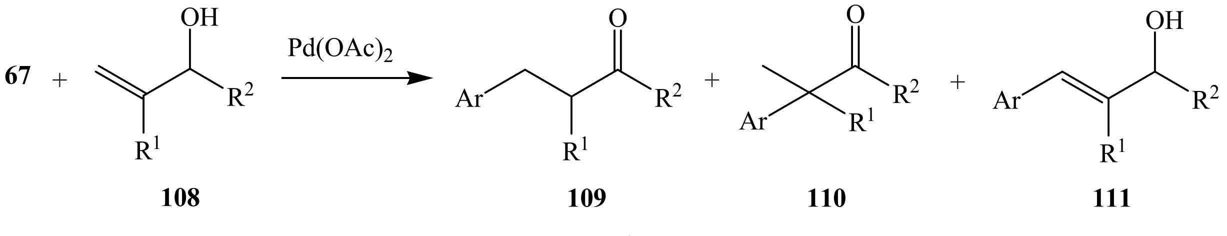
106

107

9 examples, 70–90%

Scheme 36.

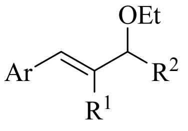
Dry arenediazonium *o*-benzenedisulfonimides were used in palladium-catalyzed arylation of allylic alcohols [53]. As known from literature, such reactions are generally poorly regiospecific and lead to mixtures of β- and α-arylated both carbonyl compounds and allylic alcohols; selective procedures have been proposed, but only a few reports refer to arylation by arenediazonium salts. Variously substituted salts **67** were reacted with a range of primary and secondary allylic alcohols, testing several reaction conditions (solvent, nature and equivalents of base and palladium catalyst). The synthetic goal were the β-arylated carbonyl compounds, useful intermediates for the synthesis of medicinal or natural products with biological properties. In optimized conditions, salts **67** and secondary allylic alcohols **108** (1.2 equiv) were reacted in aqueous 95% ethanol/$NaHCO_3$ (1.2 equiv) or acetonitrile/NaOAc (1.2 equiv), in the presence of $Pd(OAc)_2$ (1 mol%), at 60 °C; they gave β-arylated ketones **109** as major products, along with traces of α-arylated ketones **110** and minor amounts of arylated allylic alcohols **111** (Scheme 37).



Ar = Ph; 4-MeC_6H_4; 2-, 4-$MeOC_6H_4$; 4-BrC_6H_4; 4-IC_6H_4; 2,6-$F_2C_6H_3$; 2-, 3-, 4-$NO_2C_6H_4$
R^1 = H, Me
R^2 = H, Me, *n*-C_5H_{11}, Ph

Scheme 37.

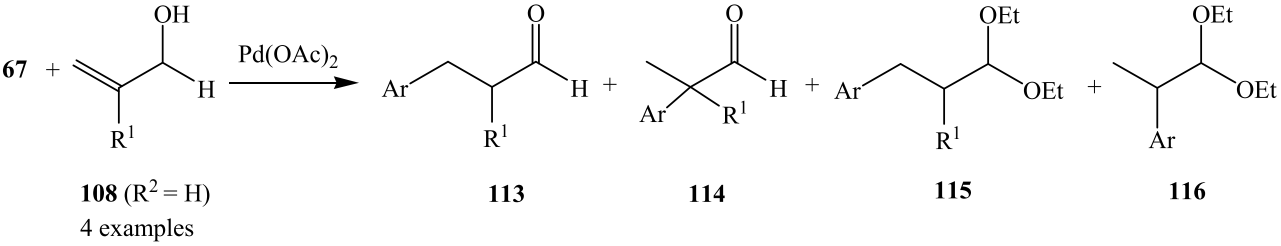
According to literature, as electron-rich haloarenes disfavour Heck-type reactions, electron-rich arenediazonium salts gave lower product yields. Furthermore, from the reaction of these salts in ethanol, the corresponding 1-aryl-3-ethoxyalk-1-enes **112** were isolated and identified by GC-MS and ^1H NMR spectra. Their formation was attributed by the authors to a nucleophilic attack of the alcoholic solvent on an intermediate π-allylpalladium complex (Tsuji–Trost reaction [54]), as confirmed by carrying out the reaction in methanol and isolating the corresponding 1-aryl-3-methoxyalk-1-enes.



112

Fig. (7).

Salts **67** and primary allylic alcohols **108** (R^2=H; 1.2 equiv) in aqueous 95% ethanol/$NaHCO_3$ (1.2 equiv), in the presence of $Pd(OAc)_2$ (1 mol%) at 60 °C, led to mixtures of arylated aldehydes **113** and/or **114** with their diethyl acetals **115** and **116** (with the expected predominance of the former ones; Scheme 38).



Scheme 38.

Palladium-catalyzed cross-coupling reactions with aryl and alkyl tin compounds, and with trialkylboranes:

In order to broaden the synthetic potential of salts **67** as aryl electrophile components in transition metal catalyzed cross-coupling reactions, a wide range of dry arenediazonium *o*-benzenedisulfonimides were reacted with aryltin derivatives **117** (1.1 equiv) under Stille conditions to give asymmetric biaryls **118**, fundamental building blocks in organic synthesis [55]. All the reactions were carried out in THF in the presence of $Pd(OAc)_2$ 5% as precatalyst, at room temperature or 40 °C for arenediazonium salts *ortho* monosubstituted; yields were always high (23 examples; average yield 80%), with the only exception of two *ortho* disubstituted salts (yields 22–23%). In these cases, more consistent amounts of symmetric biaryls **119** were isolated, otherwise present in traces (Scheme 39).

$$\mathbf{67} + \underset{\mathbf{117}}{\text{Ar'-SnBu}_3} \xrightarrow{\text{Pd(OAc)}_2} \underset{\mathbf{118}}{\text{Ar-Ar'}} + \underset{\mathbf{119}}{\text{Ar'-Ar'}}$$

23 example: **118,** 61–95%; **119**, tr–9%
2 examples: **118**, 22–23%; **119**, 30–33%

Ar = 2-, 3-, 4-MeC_6H_4; 2-, 3-, 4-$MeOC_6H_4$; 4-BrC_6H_4; 4-IC_6H_4; 4-CNC_6H_4; 4-$MeOCOC_6H_4$;
2-, 3-, 4-$NO_2C_6H_4$; 2,6-$Me_2C_6H_3$; 2,6-$(NO_2)C_6H_3$
Ar' = Ph, 4-$MeOC_6H_4$; 4-ClC_6H_4; 2,6-$Me_2C_6H_3$; 2-furyl; 2-thienyl

Scheme 39.

In contrast to numerous examples of cross-coupling reactions between arenediazonium salts and aromatic or alkenyl organometallic compounds, very few examples are reported with alkyl organometallic compounds. Salts **67** were successfully tested in such palladium-catalyzed alkylation [56]. By reaction with tetramethyl or tetrabutyltin **120** (1.1 equiv), in THF at room temperature or in acetonitrile at 40 °C, in the presence of $Pd(OAc)_2$ 2.5 mol%, chemoselective methylation and butylation products **121** and **122** were obtained in high and modest yields, respectively; the presence of arenes **123**, formed by hydrodediazoniation, was nearly always observed and often made purifications difficult (Scheme 40).

$$\mathbf{67} + R_4Sn \xrightarrow{\text{Pd(OAc)}_2} \text{Ar-R} + \text{ArH}$$

120: R = Me, Bu

121: R = Me; 13 examples**,** 68–100%
122: R = Bu; 5 examples, 15–44%

123

Scheme 40.

In order to improve product yields and to avoid the use of toxic tin derivatives, reactions of salts **67** were investigated with triethyl or tributylborane **124** (1.1 equiv) under Suzuki protocol, in THF at room temperature, in the presence of different palladium catalysts, with good yields of products **125** and **122** (Scheme 41).

$$\mathbf{67} + \underset{\mathbf{124}}{R_3B} \xrightarrow{\text{Pd cat}} \text{Ar-R} + \underset{\mathbf{123}}{\text{ArH}}$$

125: R = Et; 8 examples; 74–88%
122: R = Bu; 8 examples; 64–85%

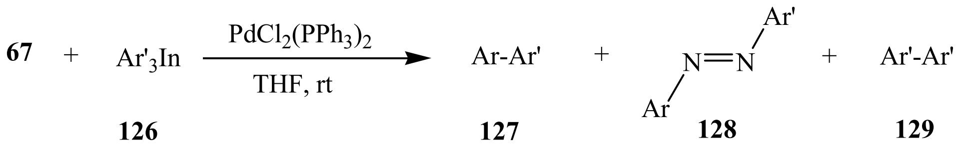
Ar = 4-MeC_6H_4; 4-$MeOC_6H_4$; 4-CNC_6H_4; 4-BrC_6H_4; 2-, 3-, 4-$NO_2C_6H_4$; 4-BuC_6H_4
R = Et, Bu

Scheme 41.

Palladium-catalyzed cross-coupling reactions with aryl and alkylindium compounds:

As a follow-up on our previous studies, dry arenediazonium *o*-benzenedisulfonimides **67** were reacted with triorganoindium compounds **126**, and depending on the reaction conditions, it was possible to obtain biaryls **127** or diaryldiazenes **128** [57]. Before this paper, no reactions of arenediazonium salts with indium organometallics have been reported in literature. Triorganoindium compounds **126** were prepared from indium(III) chloride with aryllithium or Grignard reagents.

As regards to the first synthetic application, in optimized conditions salts **67** were reacted with compounds **126** in a molar ratio 3:1, in THF at room temperature, in the presence of bis(triphenylphosphine)palladium (II) dichloride as precatalyst. Biaryls **127** were obtained in high yields, chemoselectively, independently from electronic but not steric effects (Scheme 42).

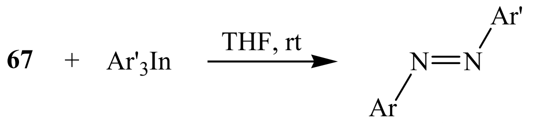


16 examples; **127**: 70–94%; **128**: tr–4%;

Ar = 4-MeC_6H_4; 2-, 3-, 4-$MeOC_6H_4$; 3-, 4-BrC_6H_4; 4-IC_6H_4; 4-ClC_6H_4; 4-$MeOCOC_6H_4$;
2-, 3-, 4-$NO_2C_6H_4$; 2,6-$F_2C_6H_3$; 2,6-$(NO_2)C_6H_3$; 4-CNC_6H_4; 2,6-$Me_2C_6H_3$;
Ar' = Ph, 4-$MeOC_6H_4$; 4-ClC_6H_4; 4-MeC_6H_4; 2-thienyl

Scheme 42.

In order to favour the electrophilic *C*-coupling reaction and maximize the yields of **128** derivatives, salts **67** were reacted with triorganoindium **126** without catalyst. In optimal conditions the molar ratio **67** : **126** was 1 : 2, in THF at room temperature. Variously substituted aryldiazenes were obtained in good yields (except for sterically hindered arenediazonium cations), comparable to those previously obtained from the same arenediazonium salts (Scheme 43) [41].



126 **128**

18 examples; 43–95%

Scheme 43.

The behaviour of salts **67** with indium triorganocompounds was investigated by reaction with other organometallic reagents, including organotin, boronic acid, Grignard and lithium compounds, in the presence or absence of Pd^0 catalyst. Results were explained by different nucleophilicities of the tested organometallic reagents.

Next, reaction of salts **67** with aliphatic triorganoindium compounds (triethyl **130**, tributyl **131** and trimethylindium **132**; 2.5 equiv, in THF at room temperature) was investigated, but quite surprisingly, aqueous treatment of reaction mixtures gave *N*-ethyl- **133** and *N*-butylanilines **134** (uncontaminated by *N,N*-dialkylanilines) or formaldehyde (aryl)hydrazones **135**, respectively [58]. Reactions were not influenced by electronic or steric effects, although hindered samples were obtained in moderate yields (Scheme 44).

$$\mathbf{67} + R_3In \xrightarrow[\text{2. } H_2O]{\text{1. THF, rt}} \text{Ar-NH-R} \quad \text{or} \quad \text{Ar-NH-N=CH}_2$$

130: R = Et
131: R = Bu
132: R = Me

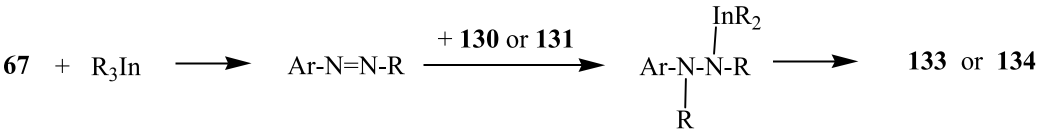
133: R = Et; 9 examples; 69–89%
134: R = Bu; 9 examples; 75–95%

135: 9 examples; 61–89%

Ar = Ph; 4-MeC_6H_4; 4-$MeOC_6H_4$; 4-BrC_6H_4; 4-$MeOCOC_6H_4$; 2-, 3-, 4-$NO_2C_6H_4$; 2,6-$Me_2C_6H_3$

Scheme 44.

The mechanism previously proposed [44] was used in part also in this case: nucleophilic addition of **130** or **131** to the intermediate aryl(alkyl)diazene on the amino nitrogen atom and decomposition of this temporary adduct lead to the end products **133** or **134**.



$$\mathbf{67} + R_3In \longrightarrow \text{Ar-N=N-R} \xrightarrow{+\,\mathbf{130}\text{ or }\mathbf{131}} \text{Ar-}\underset{\substack{|\\ R}}{N}\text{-}\overset{\substack{InR_2\\ |}}{N}\text{-R} \longrightarrow \mathbf{133}\text{ or }\mathbf{134}$$

Scheme 45.

In the case of trimethylindium **132** only formaldehyde (aryl)hydrazones **135** were obtained. Experimental results were justified by the well-known tautomerism between diazenes (I) and hydrazones (II), the latter being unable to undergo nucleophilic addition (Fig. 8).

$$\underset{\textbf{I}}{\text{Ar-N=N-CH}_2\text{R}} \rightleftharpoons \underset{\textbf{II}}{\text{Ar-NH-N=CHR}}$$

Fig. (8).

Basing our hypothesis on previously reported but not unequivocal data [59], a theoretical study was performed with detailed density functional (DFT) calculations; results confirmed the higher stability of hydrazone tautomers, shifted towards diazene tautomers by the catalytic effect of water added at the end of the reaction. The key step is the nucleophilic addition to the N=N double bond; by using three different reaction pathways, the anomalous behaviour of **132** was explained on the basis of stronger C–In bond in this organometallic reagent.

2.3 *o*-BENZENEDISULFONIMIDE as BRØNSTED ACID CATALYST

The high acidity of the Brønsted acid **1** is well-known. Hendrickson [4] and co-workers described *o*-benzenedisulfonimide as “fully ionized in (and not extractable from) water”; tabulated values for pK_a are –4.1 (H_0 at half-neutralization determined by UV spectra, at 20 °C in water [1b]), and –1.10 (calculated with the program ACD/pK_a DB [60]). However, until our recent researches, to the best or our knowledge, no one has taken advantage of this finding.

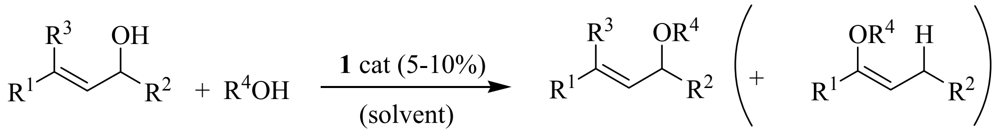
Recently, during our investigations concerning the reactivity of dry salts **67** in metal-catalyzed cross-coupling reactions [53], along with the expected mixtures of α- and β-arylated carbonyl compounds and of arylated allylic alcohols, some ethoxyderivatives **112** were isolated. Their formation was ascribed to a Pd catalyzed Tsuji–Trost reaction of ethanol on the intermediate arylated allylic alcohol. Unexpectedly, such derivatives derived from acid-catalyzed dehydration of the two cited alcohols: the strong Brønsted acid actively involved even in catalytic amounts was *o*-benzenedisulfonimide (**1**).

So far, several good results have been obtained using *o*-benzenedisulfonimide in catalytic amounts, as a safe, easy to handle, nonvolatile, non corrosive, and recyclable Brønsted acid. This organocatalyst presents many advantages: highly soluble in both organic solvents and water, efficiently catalyzes some of the most common acid-catalyzed organic reactions in homogeneous catalysis conditions, and thorough studies on other synthetic applications are in progress. As in the case of arenediazonium salts **67**, a further valuable and not negligible aspect of this catalyst is its almost complete and easy recovery after workup of the reaction mixtures. Owing to the complete solubility in water, it can be recovered virtually pure, ready to be reused in catalytic amounts in other reactions, immediately or after a fast purification on cation-exchange resin, without loss of catalytic activity, with clear economic and ecological advantages.

Dehydrative reactions:

First, the synthetic usefulness of **1** as catalyst was tested in some acid-catalyzed reactions, selected on the basis of their synthetic significance and methodological simplicity: dehydrative etherification and esterification; acetals synthesis, cleavage and interconversion; pinacol rearrangement [61a,61b]. All the reactions were conducted in open air flasks, using analytical grade solvents, the only side product being water.

Protic acid catalyzed ether synthesis by alcohol dehydration is dependent on the choice of reactants and of Brønsted acid; generally, high acid concentration and high reaction temperatures are required. In order to prepare asymmetric allylic ethers **138**, three different procedures have been set up by using *o*-benzenedisulfonimide, allylic alcohols **136** and aliphatic alcohols **137**: in solution of alcohol **137**, in THF as solvent, and under solvent-free conditions; in the last two procedures, aliphatic alcohols were used in stoichiometric ratio or in slight excess (Scheme 46).



136 **137** **138** **139** (from **136**, $R^3 = H$)

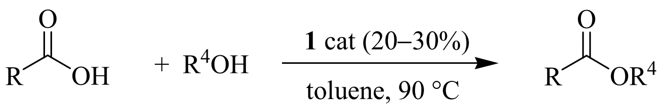
21 examples 4 examples

$R^1 = H, Me, Ph; R^2 = H, Ph$; or $R^1R^2 = –(CH_2)–_3$; $R^3 = H, Me$; $R^4 = Et$, *i*-Pr, Bn, *n*-C_8H_{17}

Scheme 46.

All methods presented mild reaction conditions, short reaction times, good selectivity (only mixed ethers were formed, no side-products were isolated), good yields (in 8 examples: 70–88%; in 8 examples: 28–60%), and reduced load of catalyst (normally 5%). When the well-known allylic rearrangement of the reasonable intermediate carbocation was allowed, ethers **139** were isolated in mixture with the isomeric ones **138**. As the reaction was an equilibrium, the conditions were optimized to lead to more stable derivatives. Furthermore, *E*-isomers always were the only isolated products. Unfortunately, *o*-benzenedisulfonimide did not play a role in such stereoselectivity: a collateral proof with sulphuric acid as catalyst gave the same results, although in lower yield.

Dehydrative esterification of carboxylic acids **140** and alcohols **137** was examined only in a few representative examples; reagents were used in nearly equimolar amounts, at 90 °C in toluene, in the presence of **1** (20–30 mol%). Our results agree with the known decreasing order reactivity of non-conjugated, conjugated and aromatic acids (Scheme 47).

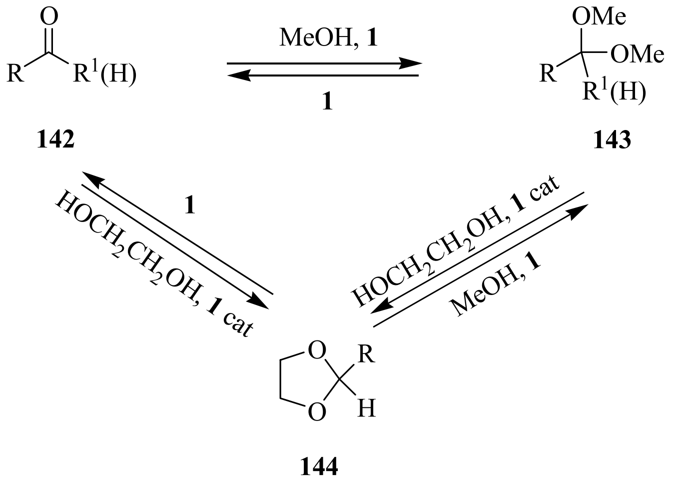


140 **137** **141**

6 examples

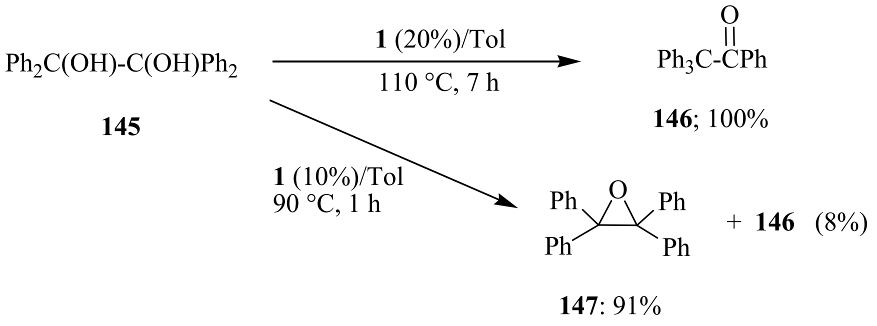
Scheme 47.

Acetalization of aldehydes or ketones is one of the most useful methods used in protective groups chemistry. Drawbacks of the reaction are excess of alcohol, removal of water, use of a toxic or corrosive acid catalyst, sometimes needed in large amounts. In our conditions, dimethyl or ethylene acetals of a number of aldehydes and/or ketones were obtained in satisfactory yields by reactions with methanol (also as solvent) or ethane-1,2-diol (3 equiv, in toluene), at room temperature or 90 °C respectively, in the presence of *o*-benzenedisulfonimide (0.5–1 mol%). In the presence of the same catalyst, some acetal cleavages and interconversions were achieved with good results (Scheme 48).



Scheme 48.

Moreover, pinacol rearrangement of 1,1,2,2-tetraphenylethane-1,2-diol **145** was studied: depending on reaction conditions, benzopinacolone **146** or tetraphenyloxirane **147** were obtained, as in Scheme 49.



Scheme 49.

In further studies, *o*-benzenedisulfonimide was taken in consideration as Brønsted acid catalyst in acylation of alcohols, phenols, and thiols with acid anhydrides [61c]. The number of recent methods reported in literature for this reaction is astonishing, and include the use of both homogeneous and heterogeneous conditions, in the presence of Brønsted or Lewis acids as catalysts. This confirms the interest in new simple, low-cost, and environmental benign procedures, involving solvent- and/or metal-free recyclable catalytic systems.

To assess the general validity of the proposed procedure, scope and limitations of the use of **1** were investigated by reacting various aliphatic and aromatic alcohols and thiols **148** (20 and 4 examples, respectively) with various anhydrides **149** (3 examples) (Scheme 50).

$$\text{(Ar)R}^1\text{-XH} \quad + \quad (\text{R}^2\text{CO})_2\text{O} \xrightarrow{\mathbf{1}} \text{(Ar)R}^1\text{-X-COR}^2$$

148 **149**: R^2 = Me, Et, Ph **150**: X = O; 23 examples; 70–100%
X = S; 4 examples; 82–100%

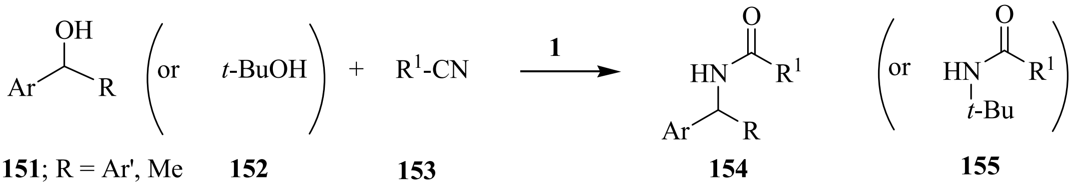
Scheme 50.

Under our optimized procedures, the conditions were very mild: nearly equimolar amounts of reagents (1 : 1.1), low and recyclable catalytic load (5 mol%), very short reaction times, room temperature (60 or 80 °C for benzoylation only), complete conversion and high yields of acylated products **150**, even in a preparation on large scale. The reaction worked well both with primary, secondary and tertiary alcohols, with stereoselectivity and without racemization of enantiomeric pure substrates; in very few cases the reaction failed, leading to a mixture of acid-catalyzed isomerization products, acylated or not.

Ritter-type reactions

The Ritter reaction is an efficient synthesis of amides from alkenes (or alcohols) and nitriles; many procedures have been achieved in the presence of Brønsted or Lewis acids, the main disadvantage being the use of toxic, corrosive, and/or expensive, and not recoverable catalysts.

By using *o*-benzenedisulfonimide as catalyst (**1**, 10 mol% for **151**, 20% for **152**), Ritter-type reaction of various benzylic alcohols **151** or *t*-butyl alcohol **152** with aliphatic or aromatic nitriles **153** (as solvent or in stoichiometric amount; in this case, only reaction rate was slowed down) gave amides **154** or **155** in good yields by heating at 100 °C or at reflux temperature (Scheme 51) [62a]. We highlight that catalyst **1** was recovered (as in all the above described procedures) and directly reused in other two consecutive Ritter-type reactions, without purification steps: reaction times showed an increase, but yields of pure isolated product and recovery of **1** were always good.



$Ar = Ph, 4\text{-}FC_6H_4, 4\text{-}MeOC_6H_4, 2,4,6\text{-}Me_3C_6H_2$
$Ar' = Ph, 4\text{-}FC_6H_4, 4\text{-}MeOC_6H_4, 4\text{-}NO_2C_6H_4, 2,4,6\text{-}Me_3C_6H_2$
$R^1 = Me, Ph, 2\text{-}, 3\text{-}, 4\text{-}MeC_6H_4, 4\text{-}MeCOC_6H_4$, vinyl

R = Ar'; 15 examples
R = Me; 6 examples

5 examples

Scheme 51.

The reactions were independent of electronic effects (13 examples: 73–99%), with regard to **153**; in contrast, steric effects reduced drastically the yield (2 examples: 30–51%). As regard to **151**, electronic effects were important and they were explained by considering the hypothesized mechanism of the reaction. By monitoring the reaction by GC-MS, formation of intermediate ethers **156** and their disappearance in favour of increase of final amides were always observed. Accordingly, the authors proposed the following catalytic cycle, where the conjugated base of catalyst **1** was omitted.

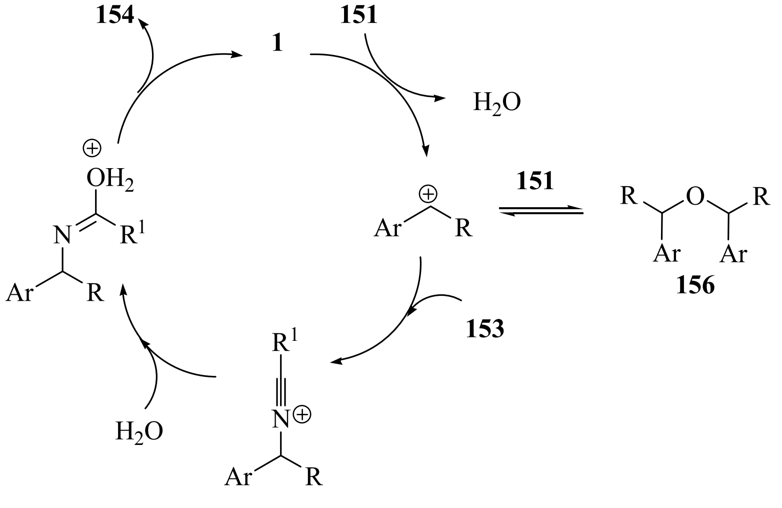
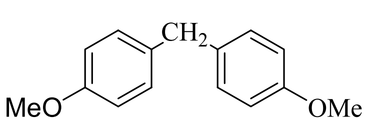


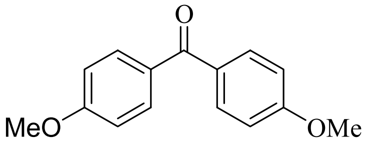
Fig. (9).

When Ar and R were 4-methoxyphenyl, no traces of the corresponding **154** were detected: only bis(4-methoxyphenyl)methane (**157**) and 4,4'-dimethoxybenzophenone (**158**) were isolated in

42 and 58% yield respectively. Under catalytic acid conditions, diarylmethyl isopropyl ethers undergo disproportionation reaction with selective hydride transfer leading to diarylmethanes and acetone [63]; therefore, **157** and **158** formation was explained by the authors as disproportionation products of the intermediate ether **156**.



157



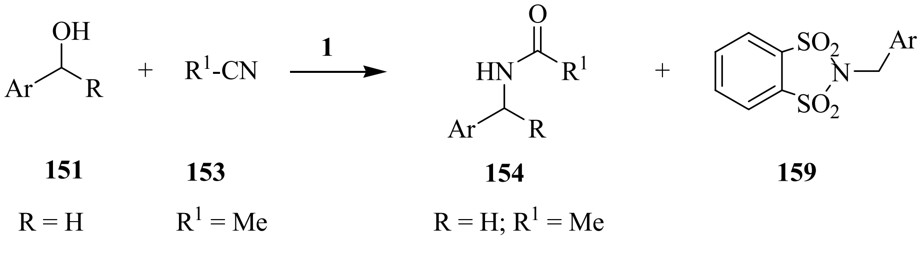
158

Fig. (10).

When R was a methyl group, vinylbenzenes as side-products were detected; electronic effects of electron-donating and electron-withdrawing groups were observed.

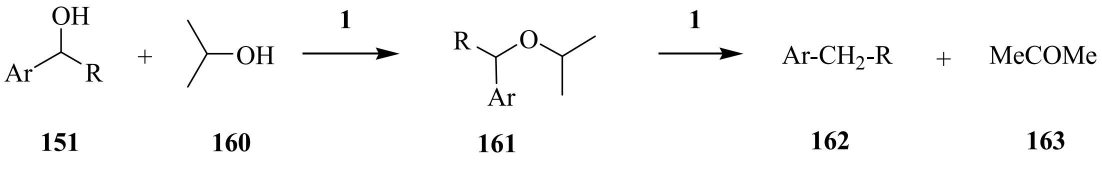
Reactions of nitriles **153** with *tert*-butyl alcohol gave satisfactory yields, with the exception of the sterically hindered 2,6-dimethylbenzonitrile.

Finally, four primary benzylic alcohols were reacted with acetonitrile: larger amounts of catalyst (until 1 equiv) was needed to obtain moderate yields of **154** (35–64%), along with nearly the same amounts of *N*-benzyl-*o*-benzenedisulfonimides **159** (28–35%), despite the known poor nucleophilicity of **1** (Scheme 52).



Scheme 52.

Bearing in mind the disproportionation products observed in this study, the authors decided to investigate more in depth the reaction, both having the synthetic goal of diarylmethanes and a theoretical study confirmation. Therefore, various ethers **161** were synthesized *in situ* by reacting diarylmethanols or benzylic alcohols **151** with propan-2-ol (**160**), in the presence of 10 mol% of **1** as catalyst, and by heating at 80 °C until the complete conversion into diarylmethanes **162** and acetone (**163**). Without electron-donating substituents on the aromatic ring the reaction did not occur, and it also failed with primary benzylic alcohols (Scheme 53).



R = Ar', H

10 examples

Scheme 53.

The theoretical study, performed within the Density Functional Theory (DFT), confirmed that the reaction proceeds through two steps: formation of a carbocation from the protonated ether followed by hydride transfer. Although the latter is the rate determining step, the whole reaction rate is determined by the stability of the carbocation: the more stable ion leads to the lower potential energy profile, the faster reaction and, therefore, the better yield of product [62b].

Nazarov electrocyclization:

The electrocyclization of divinyl ketones into cyclopentenones, the Nazarov reaction, is a versatile method for realizing cyclopentenone frameworks in more complex carbo- and heterocyclic molecules, possessing biological activities. The reaction requires acidic activation but, whilst Lewis acid catalysis is well assessed, protic acid catalysis has been less explored; in this context, the catalytic efficiency of *o*-benzenedisulfonimide was evaluated on a wide range of both activated and inactivated substrates [64]. It is well-known that the electrocyclization of dienones in cyclopentenones involves both a pentadienyl A and an hydroxyallyl cation B intermediate, as outlined in the catalytic cycle (Fig. 11).

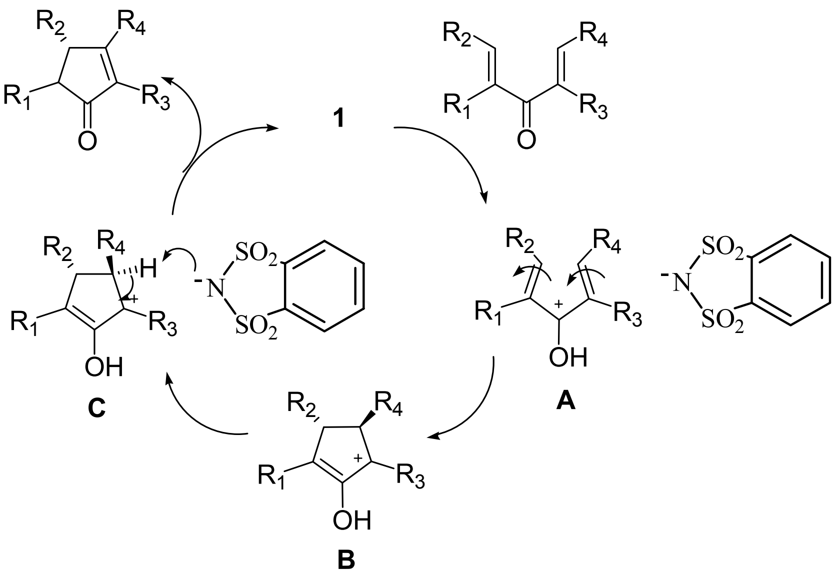
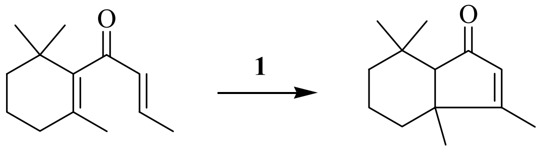


Fig. (11).

After several preliminary proofs of cyclization on β-damascone (**164**), looking for the best conditions in terms of amounts of catalyst, solvent, and temperature, a series of various eterocyclic-derived dienones were successfully cyclized in the presence of **1** in catalytic amounts, with satisfactory results, comparable with those obtained under traditional Lewis or Brønsted acid catalysts (Scheme 54).



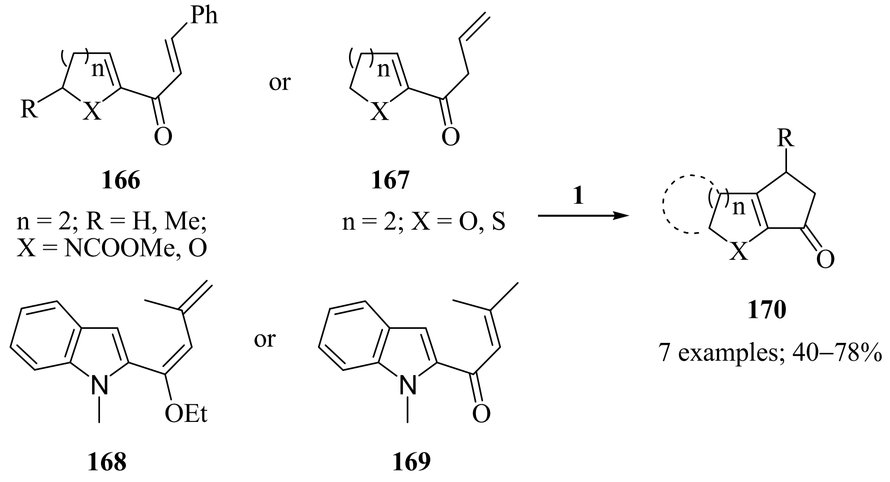
164 **165**

Scheme 54.

All the starting dienones **166**, **167**, **168**, and **169** present one of the double bonds embedded in a heterocyclic framework; they were supposed to take advantage of the presence of the heteroatom in α-position of the dienone (Scheme 55). In the case of **167**, isomerization of the terminal double bond must occur before the cyclization process takes place. Reaction conditions were optimized for each of the seven substrates (solvent, temperature, catalytic load 5–30 mol%), evidencing a strong solvent effect, as well solvent-free conditions.

With a suitable substrate (**166**, R = Me), a good diastereoselectivity was observed, with a 5 to 1 ratio in favour of the *trans*-diastereoisomer, in accord to previously obtained data, both under Brønsted and Lewis acid catalysis.

Interestingly, *o*-benzenedisulfonimide proved to be an efficient electrocyclization catalyst, also in the case of dienone **169**, where other catalysts failed. Furthermore, its recyclability was again demonstrated.



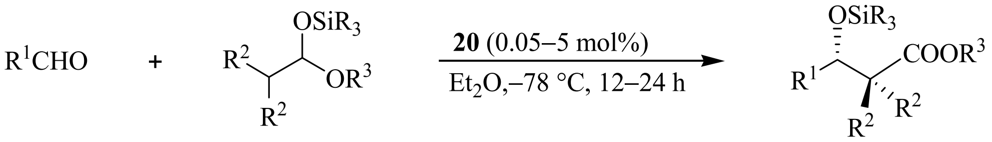
Scheme 55.

2.4 ASYMMETRIC ORGANOCATALYSIS

The most recent and significant results concerning cyclic disulfonimides chemistry have been published in the last months.

The development of new organocatalysts is of crucial importance in asymmetric organic synthesis and many Lewis and Brønsted acids (and bases) have been proposed as useful organocatalysts in numerous organic transformations. In particular, very strong chiral Brønsted superacids have attracted the attention of chemists as promising catalysts because of their higher reactivity in the activation of substrates of low basicity, and the chiral environment induced by the corresponding chiral conjugated bases [65a] (concept also expressed as Asymmetric Counteranion Directed Catalysis, ACDC [65b]).

In this context, chiral disulfonimides **20** and **21** have been synthesized as new chiral strong Brønsted acids [15,16], and **20** has been shown to catalyze the asymmetric Mukaiyama aldol reaction with high efficiency, high enantioselectivity and turnover numbers of up to 8800 [15]. (*R*)-3,3’-Bis[3,5-bis(trifluoromethyl)phenyl]-1,1’-binaphthyl-2,2’-disulfonimide (**20**) was used in catalytic amounts (2–0.01 mol%) with good to excellent yields of aldol products **173** and high enantioselectivity (8 examples). In the presence of 5 mol% of catalyst, also aliphatic aldehydes gave good yields of products and reasonably good enantioselectivity (2 examples) (Scheme 56).



171 **172** **173**

R^1 = Ar, styryl, alkyl R^2 = H, Me; R^3 = Me, *i*-Pr **173**: 8 examples (**20**, 2 mol%); 78–98% (86 : 14–97 : 3% e.r.)
2 examples (**20**, 5 mol%); 46–59% (75 : 25–91 : 9% e.r.)

Scheme 56.

Moreover, catalyst **20** resulted to be more active and efficient than other known chiral binaphthyl acidic derivatives in the catalysis of asymmetric Mukaiyama aldol reaction, thus opening new promising perspectives of applications in asymmetric organic transformations.

3. CRYSTAL STRUCTURE STUDIES ON *o*-BENZENEDISULFONIMIDE DERIVATIVES

Since molecules containing the sulfonimide [$(SO_2)_2NH$] moiety are strong NH acids, they can form with base either onium salts or uncharged hydrogen-bonded complexes. In literature, there is a substantial number of papers, mainly by A. Blaschette and P. J. Jones, from 1993 [5], that report crystal structures of such derivatives with *o*-benzenedisulfonimide (**1**), belonging to both classes of compounds, normally prepared by metathesis from silver(I) *o*-benzenedisulfonimide (**29**) or by **1** directly. In Table 1, we reported a list of studied onium compounds or coordination complexes in a chronological order.

Table 1.

]

Compounds	Lit. Ref.	Compounds	Lit. Ref.
$C_6H_4(SO_2)_2NAg \cdot CH_3CN$	[5]	$Me_2[C_6H_4(SO_2)_2N]_2Sn(OPPh_3)_2$ and $[Me_2Sn(phen)_2][C_6H_4(SO_2)_2N]_2 \cdot CH_3CN$	[75]
$C_6H_4(SO_2)_2NAg \cdot H_2O$	[66]	$C_6H_4(SO_2)_2NH$ and $C_6H_4(SO_2)_2NCs$	[76]
$[C_6H_4(SO_2)_2N]_2SnMe_2(H_2O)_4$	[67]	$C_6H_4(SO_2)_2NK \cdot H_2O$, $C_6H_4(SO_2)_2NRb \cdot H_2O$, $C_6H_4(SO_2)_2NNH_4 \cdot H_2O$	[77]
$\{Me_2[C_6H_4(SO_2)_2N]Sn(\mu\text{-}OH)\}_2$	[68]	$C_6H_4(SO_2)_2NNa \cdot H_2O$	[78]
$C_6H_4(SO_2)_2NAuPPh_3O$	[69]	$C_6H_4(SO_2)_2NLi(H_2O)_3$	[79]
$[C_6H_4(SO_2)_2N]_2Ca(H_2O)_7$	[70]	$[C_6H_4(SO_2)_2N]_2Cd_2(H_2O)_4$ and $[C_6H_4(SO_2)_2N]_2Cu(H_2O)_4$	[80]
$[C_6H_4(SO_2)_2NLi(12\text{-crown-}4)]$	[71]	$[C_6H_4(SO_2)_2N]_2Mg(H_2O)_6$ and $[C_6H_4(SO_2)_2N]_2Be(H_2O)_4 \cdot 2\ H_2O$	[81]
$[C_6H_4(SO_2)_2NNa(15\text{-crown-}5)]$	[72]	$[C_6H_4(SO_2)_2N]_2Ba(H_2O)_2$	[82]
$C_6H_4(SO_2)_2NH \cdot CH_3CN$	[73]	$C_6H_4(SO_2)_2NNH_4 \cdot H_2O$ and $C_6H_4(SO_2)_2N[Ph_3PNPPh_3]$	[60]
$C_6H_4(SO_2)_2NAu(CyNH_2)_2$	[74]		

The crystal structure of *o*-benzenedisulfonimide itself was determined: the five membered 1,3,2-dithiazole ring has an envelope conformation, with the N atom lying outside the mean plane of the S–C–C–S moiety; in the crystal, the molecules are linked by N–H…O hydrogen bonds into chains and in a three-dimensional network [73,74]. The structure of the conjugated anion is described as an essentially planar bicyclic framework [67,72,73,74].

4. USES AND APPLICATIONS

Some of the uses below have only a historical interest. Prepared by Holleman as saccharine analogue, sweetener properties of the *o*-benzenedisulfonimide were tested: it “has at once a sweet and acid taste with a bitter after taste”[2]; however, the replacement of the imide hydrogen by an alkyl group led to practically tasteless compounds [83].

N-Alkyl and *N*-dialkylaminoalkylderivatives have been reported to have local anaesthetic activity, more effective intradermally than by topical application [19]. 2-Methyl-5-chloro-6-methylsulfamoylbenzo-1,3,2-dithiazole 1,1,3,3-tetraoxide showed diuretic activity [84]. A disulfonimide coumarin derivative is a bleach-resistant fluorescent whitener [85]. A *N*-aryl disulfonimide derivative has been copolymerized with acrylonitrile and methyl methacrylate to produce a useful fibre with permanent antistatic properties [86]. Heat-resistant polymers comprising poly(phenylene ethers), optionally styrene polymers and imides showed improved moldability [87].

5. CONCLUSIONS

o-Benzenedisulfonimide proved to be a useful reagent in organic synthesis. As outlined in the most recent studies, compared to strong liquid or solid Brønsted acids, extensively used from research laboratories to chemical manufacturing plants, the potential applications of **1** as safe, easy to handle, non corrosive, recoverable and recyclable organocatalyst are practically unlimited. Moreover, in the prospect of designing new chiral organocatalysts, investigations on new synthetic applications and structural modifications of **1** have gained the chemists attention and unprecedented results in asymmetric Mukaiyama aldol reaction have been recently reported.

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