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Review

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Arenediazonium sulfonates: synthesis, comparison of structural and physicochemical properties

Aromatic diazonium salts are important building blocks in organic synthesis. The present review is concerned with such aromatic diazonium sulfonates as tosylates, dodecylbenzenesulfonates, triflates, camphorsulfonates, silica sulfates. The first part of the review provides information on the synthesis and application of these diazonium salts. It is shown that these diazonium compounds are easily synthesized by diazotization of anilines with sodium nitrite or alkyl nitrites in the presence of corresponding sulfonic acids with high yields. These diazonium salts have found wide application in the synthesis of aromatic azides, halides, triazenes, azo dyes, stilbenes, biaryls, etc. The second part of the article presents information on the comparison of the results of X-ray analysis, infrared spectroscopy and thermal analysis. The structure of diazonium sulfonate salts corresponds to the structure of classical diazonium salts (chlorides, sulfates, tetrafluoroborates). A significant difference between arenediazonium sulfonates and other diazonium salts is their explosion safety and stability in an individual form. Arenediazonium tosylates, triflates and camphorasulfonates are easily soluble both in water and in polar organic solvents. Arenediazonium dodecylbenzenesulfonates are soluble in nonpolar organic media. These features of sulfonate salts are paramount for distinguishing characteristics of the effect of the acid anion on the stability, solubility and reactivity of diazonium salts.

Keywords: diazonium salts, diazotization, sulfonates, tosylate, triflate, camphorsulfonate, silica-sulfate, dodecylbenzenesulfonate, X-Ray.

Content

List of abbreviations

KI: potassium iodide
$NaNO_2$: sodium nitrite
DSC: differential scanning calorimetry
DTA: differential thermal analysis
TGA: thermal gravimetric analysis
ADT: arenediazonium tosylates
EtOH: ethanol
MeOH: methanol
AcOH: acetic acid
DMSO: dimethyl sulfoxide
IR: infrared spectroscopy
NMR: nuclear magnetic resonance

CCl_4: carbon tetrachloride
Et_2O: diethyl ether
$ArN_2^{+}\,{}^{-}Cl$: arenediazonium chloride
$ArN_2^{+}\,{}^{-}BF_4$: arenediazonium tetrafluoroborate
$ArN_2^{+}\,{}^{-}OTf$: arenediazonium trifluoromethanesulfonate (triflate)
$ArN_2^{+}\,{}^{-}OTs$: arenediazonium p-toluenesulfonate (tosylate)
ArN_2^{+} p-$C_{12}H_{25}C_6H_4SO_3^{-}$: arenediazonium dodecylbenzenesulfonate
$ArN_2^{+-}OSO_2Camph$: arenediazonium camphorsulfonate
$ArN_2\,{}^{+-}OSO_3$-SiO_2: arenediazonium silicosulfate
$ArN_2^{+-}N(SO_2)_2Ph$: arenediazonium o-benzenedisulfonimides
MeCN: acetonitrile
THF: tetrahydrofuran
CH_2Cl_2: dichloromethane
$CHCl_3$: chloroform
H_2O: water
HCO_2H: formic acid

Review Plan

Inclusion and Exclusion Criteria: The present review is concerned with such aromatic diazonium sulfonates as tosylates, dodecylbenzenesulfonates, triflates, camphorsulfonates, silicosulfates, their synthesis and comparison of their structural characteristics.

The review data are based on scientific publications from 1936 to 2021. Some old literature sources (1936–1980) provide information about the first attempts to synthesize diazonium sulfonate salts. A large-scale study of diazonium sulfonate salts began with the work of Barbero (1998) and continues now. We searched and analyzed articles from Scopus, Web of Science, Reaxys, Sci-Finder. The keywords used for the search were ‘arenediazonium salts’, ‘sulfonates’, ‘diazotization’, ‘sulfonic acid’, etc. The resultant data were described in this article. No statistical methods were used.

Introduction

Aromatic diazonium salts are of undoubted interest in modern organic synthesis. A huge number of reviews, monographs and articles in highly rated journals have been published on the synthesis of arenediazonium salts and the study of their chemical properties. The salts discovered by Griss in 1858 [1] became a huge impetus for the development of organic synthesis: The production of azo dyes, medicines, the synthesis of halogen and azide-derived benzenes, stilbenes, diaryls, the immobilization of biodegradable polymers, nanoparticles, etc. Approximately every 10–20 years, scientists discovered new transformations of diazonium salts (Figure 1) [1]:

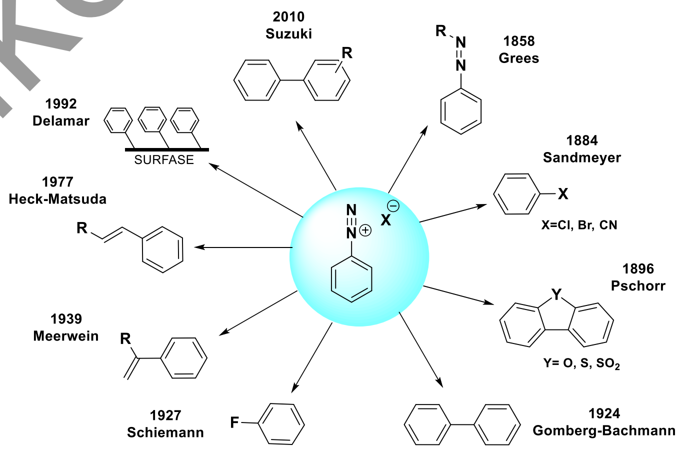


Figure 1. Transformations of diazonium salts [1]

Despite the widespread application of diazonium salts in modern organic synthesis, significant problems of their usage on an industrial scale are instability, explosiveness, non-selectivity of transformations and poor solubility in water or organic solvents. Many diazonium salts are thermally unstable and sensitive to friction and shock. Most diazonium salts are known for their violent decomposition hazard in the solid-state. This group of chemicals causes many industrial and laboratory incidents. For solving this problem, scientists are developing new types of arenediazonium salts that differ in structure only by the nature of the diazo-anion (residues of mineral or organic acids). In recent decades, obtaining and using aromatic diazonium salts of the sulfonate type devoid of most of the disadvantages of classical diazonium salts has been actively developing. This review aims to study synthesis methods of arenediazonium sulfonates and compare their physicochemical properties.

1 Diazotization in the presence of sulfonic acids

The addition of aryl sulfonic acids has a significant effect on the stability of diazonium ions [2]. This influence has been described in many patents [3]. It has been shown that the addition of α- and β-naphthalenesulfonic acids to a solution of bisdiazotized benzidine and *p*-nitrodiazobenzene leads to the formation of precipitates, which can be filtered off and dried without any danger. These products easily dissolve in water and enter reactions characteristic of diazonium ions after long-term storage.

In later works, one-stage diazotization-iodination reactions of a wide range of aromatic and heterocyclic amines under the action of the system KI/$NaNO_2$, *p*-toluenesulfonic acid in acetonitrile [4], and aqueous paste [5] were demonstrated. These methods provided high yields of the target aryl iodides and were widely used [6–9]. Before these works [5, 6], individual representatives of arenediazonium sulfonates were known, namely arenediazonium naphthalenesulfonates [10], *p*-toluenesulfonates (tosylates) [11, 12], trifluoromethanesulfonates (triflates) [13–15]; arenediazonium methanesulfonates (mesylates obtained in solution but not isolated individually) [16] (Figure 2).

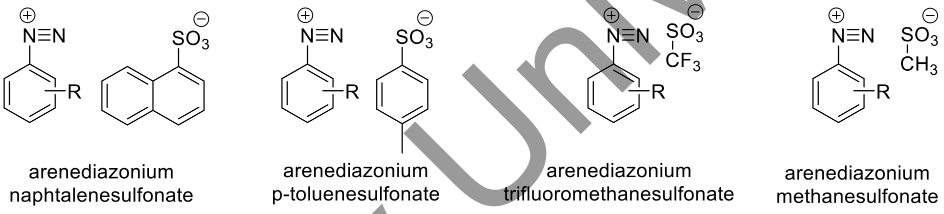


Figure 2. Some examples of diazonium sulfonate salts

1.1 Synthesis of arenediazonium tosylates, triflates, mesylates and dodecylbenzenesulfonates

Historically, the first method for preparing arenediazonium sulfonates was the decomposition reaction of arendiazonium chlorides in the presence of aromatic sulfonic acids [3]. In this case, it was necessary to resort to rubbing unsafe dry arenediazonium chlorides. This method was used to obtain some benzenediazonium salts of α-, β-naphthalene and α-, β-anthraquinone sulfonic acids [17].

Later, this approach was used to obtain some tosylates (Figure 3) [17] and 2-(trifluoromethoxy) biphenyl-2'-diazonium triflate (Figure 4) [18].

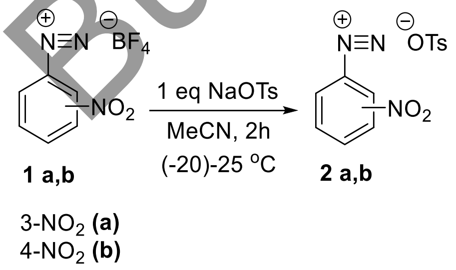


Figure 3. Obtaining arenediazonium tosylates

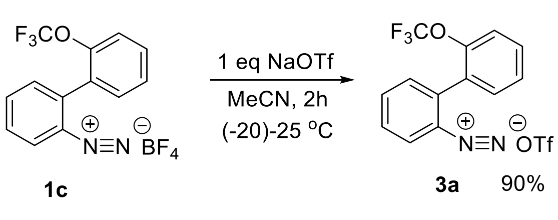


Figure 4. Obtaining arenediazonium triflate

Some arenediazonium tosylates and triflates were obtained by direct diazotization of anilines with alkyl nitrites in the presence of *p*-toluenesulfonic acid [19–21] and trifluoromethanesulfonic acid [19] in a solution of acetic acid or a mixture of tetrahydrofuran-acetic acid, respectively (Figure 5).

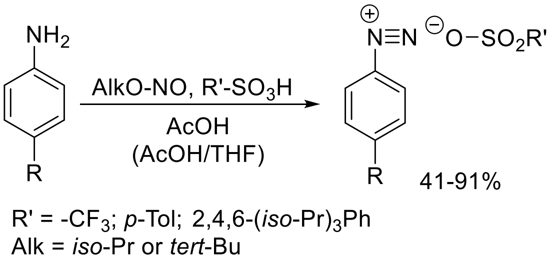


Figure 5. Preparation of arenediazonium tosylate and triflate in the presence of alkyl nitrites

Arenediazonium mesylates were obtained *in situ* with the use of methanesulfonic acid [16] and used as a solution in further transformations (Figure 6).

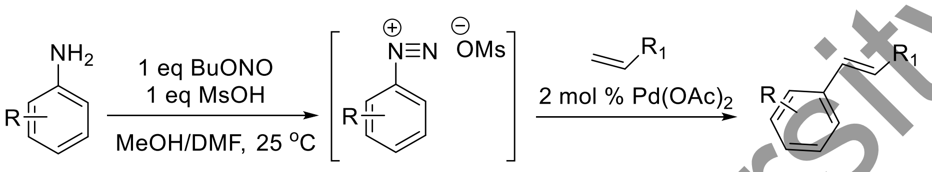


Figure 6. Preparation and transformation of arenediazonium mesylates *in situ*

Some examples of arenediazonium triflates were obtained by indirect methods [13, 14]. These methods were based on N-substituted aniline azodesilylation under the action of NO$^+$CF$_3$SO$_3^-$ and led to the formation of benzenediazonium trifluoromethanesulfonate in 93 % yield [13] (Figure 7).

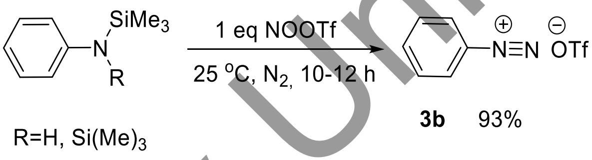


Figure 7. Azodesilylation of N-substituted aniline under the action of NO$^+$ CF$_3$SO$_3^-$

Para-substituted benzenediazonium trifluoromethanesulfonates were synthesized by treating the corresponding triazenes with 2 trifluoromethanesulfonic acid [14] (Figure 8).

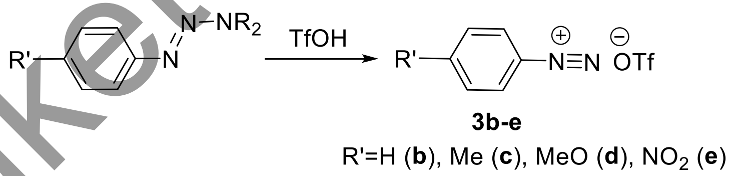
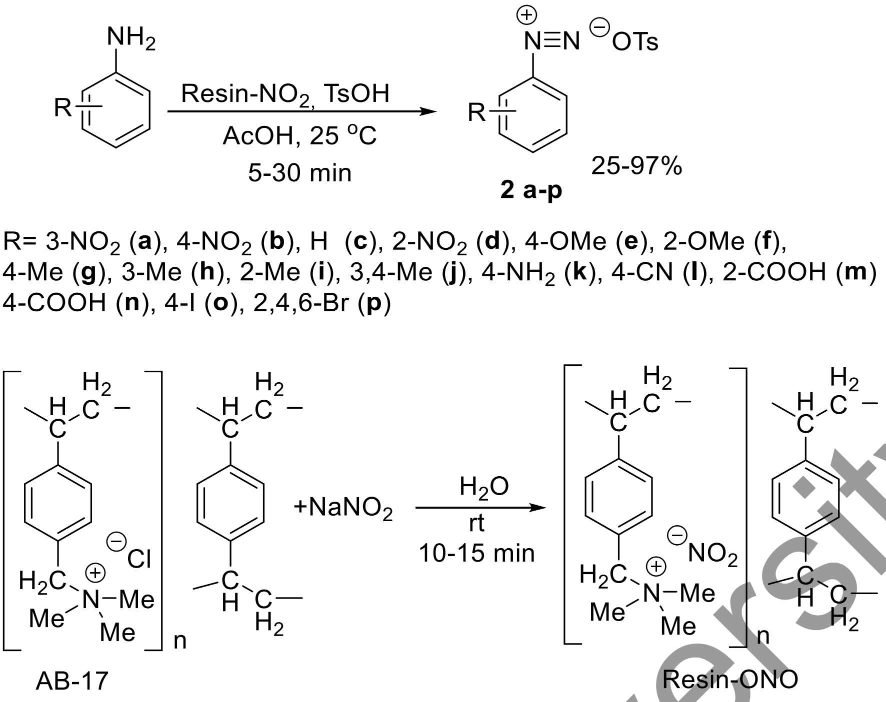


Figure 8. Synthesis of benzenediazonium trifluoromethanesulfonates via the corresponding triazenes

It should be noted that none of these works [10–21] set the task of a detailed study of the structure and physicochemical properties of arenediazonium sulfonates. This problem was partially solved in the study conducted by Filimonov V.D. et al. [21]. They developed an efficient method for the preparation of arenediazonium tosylates [21] using a new diazotizing agent with a polymer structure (Figure 9). Diazotization proceeded in acetic acid at room temperature; the formed diazonium salt was precipitated with diethyl ether. Initially, cheap sodium nitrite was used as a diazotizing agent [22]; however, in this case, the target products were contaminated with an admixture of the sodium salt of *p*-toluenesulfonic acid. The method provided the synthesis of a wide range of arenediazonium tosylates, which made it possible to conduct a detailed study of their physicochemical properties.

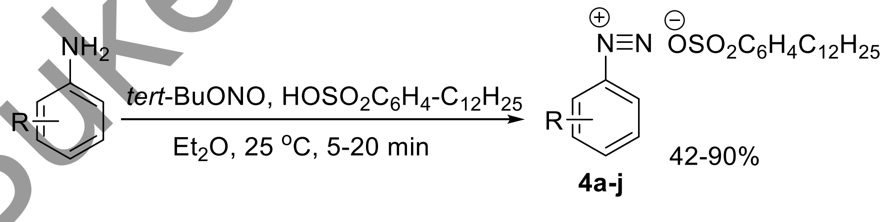


R= 3-NO_2 (**a**), 4-NO_2 (**b**), H (**c**), 2-NO_2 (**d**), 4-OMe (**e**), 2-OMe (**f**), 4-Me (**g**), 3-Me (**h**), 2-Me (**i**), 3,4-Me (**j**), 4-NH_2 (**k**), 4-CN (**l**), 2-COOH (**m**) 4-COOH (**n**), 4-I (**o**), 2,4,6-Br (**p**)

Figure 9. Preparation of arenediazonium tosylates using a new diazotizing agent with a polymer structure

It turned out that all synthesized arenediazonium tosylates are explosion-proof and have storage stability that is unique for diazonium salts (established using DSC/DTA/TGA). In contrast to the known arenediazonium chlorides, sulfates, and tetrafluoroborates, ADT have good solubility both in water and in organic solvents (EtOH, MeOH, AcOH, and DMSO). Furthermore, the structure of all salts was investigated and reliably established by modern physicochemical methods (X-Ray, IR, NMR spectroscopy). Thus, new unique representatives of the class of aromatic diazonium salts, namely arenediazonium tosylates, were obtained. These salts immediately found wide application in organic synthesis: preparation of aromatic iodides [5, 22], arenes containing radioisotope of fluorine [23], aryltriethylsilanes [20], aromatic azides [24], in the synthesis of heterocyclic systems [25], modification of nanosurfaces [26, 27], in the Heck reaction [28].

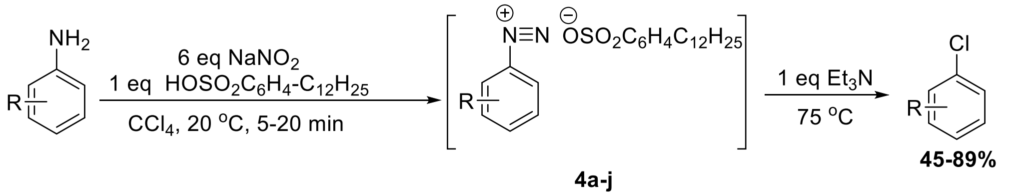
Later, this scientific group synthesized unique in their properties arenediazonium dodecylbenzenesulfonates [29]. The synthesis was based on the diazotization of anilines with *tert*-butyl nitrite and dodecylbenzenesulfonic acid in diethyl ether at room temperature.



R= H (**a**), 2-NO_2 (**b**), 3-NO_2 (**c**), 4-NO_2 (**d**), 4-OMe (**e**), 2-Br-4-NO_2 (**f**), 4-COOMe (**g**), 2-Cl (**h**), 2-Me (**i**), 4-Br (**j**)

Figure 10. Preparation of arenediazonium dodecylbenzenesulfonates

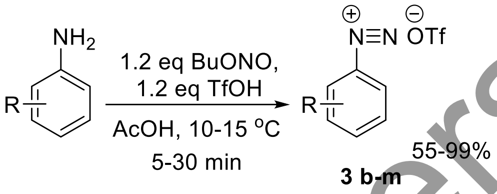
IR and NMR spectroscopy proved the structures of the synthesized salts. All synthesized salts turned out to be explosion-proof (DSC/DTA/TGA), stable during storage and having an “abnormally” high solubility for diazonium salts: Not only in water and polar organic solvents (EtOH, MeOH, AcOH, DMSO) but also in low-polarity chloroform and CCl_4. The latter circumstance provided a specific feature of the chemical behavior of these salts. Along with the reactions typical of aromatic diazonium salts (interaction with KI, combination with 2-naphthol), a previously unknown reduction to chlorobenzenes in a CCl_4 solution in the presence of a base was observed [30]. One-pot diazotization-dediazotization reaction was carried out in a CCl_4 solution under the action of sodium nitrite (Figure 11).



R= H (**a**), 2-NO_2 (**b**), 3-NO_2 (**c**), 4-NO_2 (**d**), 4-OMe (**e**), 2-Br-4-NO_2 (**f**), 4-COOMe (**g**), 2-Cl (**h**), 2-Me (**i**), 4-Br (**j**)

Figure 11. Reduction of arenediazonium dodecylbenzenesulfonates to chlorobenzenes in a CCl_4

The authors of the work [31] proposed a convenient method for the synthesis of a wide range of arenediazonium triflates by diazotization of aromatic amines with butyl nitrite in the presence of trifluoromethanesulfonic acid in acetic acid (Figure 12). A detailed study of the physicochemical characteristics of the obtained diazonium salts and their chemical transformations were carried out in the work.



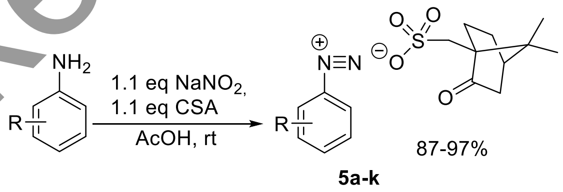
R=H (**b**), 4-Me (**c**), 4-OMe (**d**), 4-NO_2 (**e**), 3-NO_2 (**f**), 4-COOH (**g**)
4-n-Bu (**h**), 4-I (**i**), 2,4,6-I (**j**), 4-Ph (**k**), 4-NH_2 (**l**), 2-NO_2 (**m**)

Figure 12. Synthesis of arenediazonium triflates

The authors have shown that arenediazonium triflates are highly soluble both in water and in polar and low-polar organic media, explosion-proof, and stable at room temperature.

1.2 Synthesis of arenediazonium camphorsulfonates, silicasulfates, biodegradable cellulose-sulfonate, o-benzenedisulfonimides

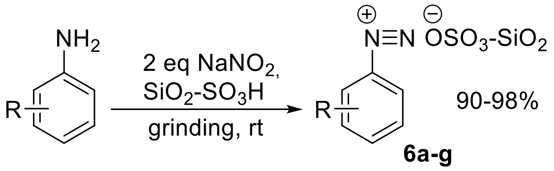
In work [32], it has recently been described the preparation of a wide range of arenediazonium camphorsulfonates through diazotization of anilines under the action of $NaNO_2$ in the presence of camphor sulfonic acid in AcOH solution at room temperature (Figure 13). It has been shown that arenediazonium camphorsulfonates can be successfully used for the preparation of aryl halides (chlorides, bromides, iodides), while the authors propose a one-stage diazotization-halogenation method both in solution (acetic acid or acetonitrile) and in the absence of a solvent.



R= 4-NO_2 (**a**), 3-NO_2 (**b**), 2-NO_2 (**c**), 4-CN (**d**), 2-CN (**e**), 4-Br (**f**),
2-Br (**g**), 4-Cl (**h**), 4-I (**i**), 4-I (**j**), 4-OMe (**k**)

Figure 13. Preparation of arenediazonium camphorsulfonates

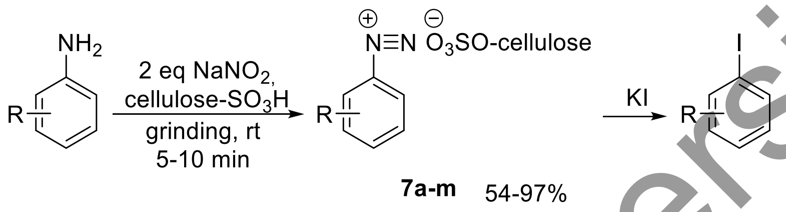
A number of works were devoted to the preparation and usage of arenediazonium silicosulfates in organic synthesis [33–38]. According to [34], diazotization of anilines with sodium nitrite in the presence of silica sulfonic acid at room temperature gave stable diazonium salts (Figure 14). These salts can be used to obtain azo dyes [34] (a method corresponding to the principles of Green Chemistry), iodoarene [33], aromatic azides [35, 36], in the reactions of C-C-coupling of Suzuki-Miyuara [37], Matsuda-Heck [38].



R=H (**a**), 2-NO_2 (**b**), 4-NO_2 (**c**), 4-SO_3Na (**d**), 2-Cl (**e**), 3-Cl (**f**), 2-Me (**g**)

Figure 14. Preparation of arenediazonium silicosulfates

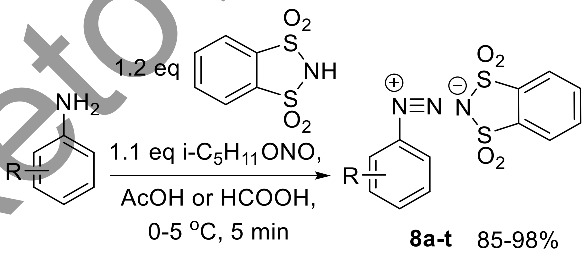
Stable aromatic diazonium salts can be synthesized by using biodegradable sulfonated cellulose (Figure 15) [39]. Diazotization proceeds mildly for 5–10 minutes at room temperature, while sulfonated cellulose can be recycled at the end of the synthesis and reused. The diazonium salts obtained easily gave the corresponding iodides and azides with quantitative yields.



R=H (**a**), 2-I (**b**), 2-COOH (**c**), 3-COOH (**d**), 4-COOH (**e**), 2,4-Cl (**f**), 3,4-Cl (**g**)
4-Cl (**h**), 4-Br (**i**), 4-OMe (**j**), 4-Me (**k**), 4-NO_2 (**l**), 2-NO_2 (**m**)

Figure 15. Using biodegradable sulfonated cellulose for diazotization

The preparation of dry arenediazonium *o*-benzenedisulfonimides was easily carried out by diazotization of aromatic amines with *i*-pentyl nitrite in the presence of *o*-benzenedisulfonimide in glacial acetic acid or in formic acid at 0–5 °C [40] (Figure 16). Using acetic acid as a solvent allows obtaining quickly a product by simple precipitation with diethyl ether. Formic acid as a solvent dissolved the diazonium salt well. Therefore, a large amount of diethyl ether was necessary for its isolation. In both solvents salts were obtained dry in high purity and excellent yields.



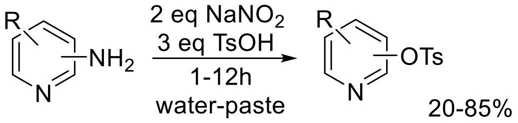
R=H (**a**), 2-Me (**b**), 3-Me (**c**), 4-Me (**d**), 2-OMe (**e**), 3-OMe (**f**), 4-OMe (**g**), 2-Cl (**h**), 3-Cl (**i**), 4-Cl (**j**),
3-Br (**k**), 4-Br (**l**), 2-NO_2 (**m**), 3-NO_2 (**n**), 4-NO_2 (**o**), 4-NMe_2 (**p**), 2,6-Me (**q**), 2-OMe-5-Cl (**r**), 2,6-Cl (**s**),
1-naphtyl (**t**)

Figure 16. Preparation of arenediazonium *o*-benzenedisulfonimides

1.3 Diazotization of aminopyridines in the presence of sulfonic acids

An attempt to use the method described above to obtain heteroaromatic diazonium salts, in particular, from aminopyridines, was unsuccessful: diazotization proceeded slowly and the corresponding hydroxypyridines were the only reaction products [41].

However, diazotization of aminopyridines under the action of sodium nitrite in the presence of *p*-toluenesulfonic acid in an aqueous paste [41] radically changed the result of the reaction. Pyridyl tosylates were isolated as the main products (Figure 17).



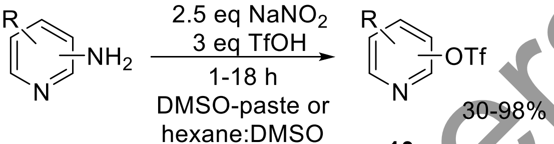
9 a-k

R=H, 2-NH_2 (**a**), 3-NH_2 (**b**), 4-NH_2 (**c**), R=5-Br, 2-NH_2 (**d**), R=5-I, 2-NH_2 (**e**),
R= 3,5-Br, 2-NH_2 (**f**), R=3-Me, 2-NH_2 (**g**), R=4-Me, 2-NH_2 (**h**), R= 6-Me, 2-NH_2 (**i**)
R= 4-Me, 5-I, 2-NH_2 (**j**), R= 2,6-NH_2 (**k**)

Figure 17. Preparation of pyridyl tosylates by direct diazotization of aminopyridines

This was the first example of the preparation of pyridyl tosylates — important intermediates in organic synthesis — by direct diazotization of aminopyridines.

Direct diazotization of aminopyridines in the presence of trifluoromethanesulfonic acid in a DMSO-paste [42] or a mixture of solvents DMSO: hexane [43] (Figure 18) made it possible to obtain more valuable pyridyl triflates widely used in modern synthesis [44].

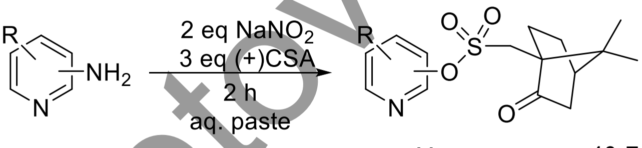


10a-m

R=H, 2-NH_2 (**a**), 3-NH_2 (**b**), 4-NH_2 (**c**), R=5-Cl, 2-NH_2 (**d**), R=6-Me, 2-NH_2 (**e**),
R=5-Br, 2-NH_2 (**f**), R=5-NO_2, 2-NH_2 (**g**), R=4-Me, 2-NH_2 (**h**), R= 2-Cl, 3-NH_2 (**i**)
R= 3,5-Br, 2-NH_2 (**j**), R= 5-I, 2-NH_2 (**k**), R=H, 2,6-NH_2 (**l**), R= 3,5-I, 2,6-NH_2 (**m**)

Figure 18. Preparation of pyridyl triflates by direct diazotization of aminopyridines

Recently, a method has been proposed for the synthesis of pyridyl camphorasulfonates, which are of interest as biologically active substances [45]. The synthesis was based on the diazotization of aminopyridines in the presence of camphor sulfonic acid in an aqueous paste (Figure 19).



11a-g 40-70 %

R=H, 2-NH_2 (**a**), 3-NH_2 (**b**), 4-NH_2 (**c**), R=5-Cl, 2-NH_2 (**d**), R=6-Me, 2-NH_2 (**e**),
R=5-Br, 2-NH_2 (**f**), R=5-NO_2, 2-NH_2 (**g**)

Figure 19. Preparation of pyridyl camphorasulfonates

This difference between aminopyridines and anilines in the diazotization reaction is due to the fact that the resulting pyridinediazonium sulfonates are thermodynamically unstable and short-lived, unlike arenediazonium sulfonates. The pyridinediazonium cations decay with the loss of nitrogen and the formation of pyridyl cations, which are highly reactive and easily interact with all nucleophiles in solution (Figure 20). This fact has been confirmed both experimentally [41, 42] and by computational methods [46].

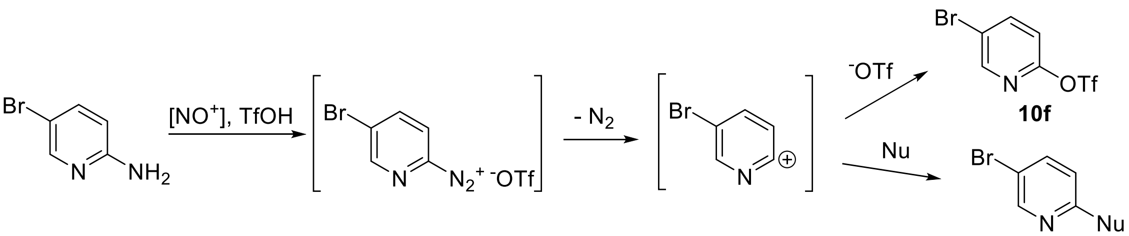


Figure 20. Plausible reaction pathways for the diazotization of 5-bromo-2-aminopyridine

Thus, arenediazonium sulfonates are easily synthesized by diazotization with sodium nitrite or alkyl nitrites in the presence of corresponding sulfonic acids with high yields. These diazonium salts have found wide application in the synthesis of aromatic azides, halides, triazenes, azo dyes, stilbenes, biaryls, etc.

2 Comparison of spectral and thermal characteristics of arenediazonium sulfonates

Comparison of the structure of aromatic diazonium salts is based on the valence oscillation of the N≡N bond in IR, the chemical shift of C_{ipso} in NMR and the results of X-ray diffraction analysis. The chemical shift of C_{ipso} carbon for all diazonium salts is in close ranges and does not correlate with the type of anion. In the IR spectrum, the valence oscillation of the diazonium group N≡N is in the characteristic region of 2100–2300 cm^{-1}.

In this review, the comparison of arenediazonium sulfonates is based on their solubility, the results of X-ray and thermal analysis. Table 1 shows the key geometric parameters, the crystallographic data, and the results of thermal analysis and information about solubility.

Table 1

The properties of some diazonium salts

No.	Name of the diazo compound	Distance C-N	Distance N-N	Angle C-N-N	Decomposition energy, kJ/mol	The solubility	Ref.
1	$ArN^{+}_{2}{}^{-}Cl$	1.385[1]	1.097	180	No information. Explosive	Soluble in water	[2]
2	$ArN^{+-}BF_4$	1.415[2]	1.083	179.5	−229.2 (at 146.5 °C) explosive	Slightly soluble in water and organic compounds	[47]
3	$ArN_2{}^{+-}OTf$	1.405[3]	1.089	178.99	From –136.1 to –840.4 non-explosive	Soluble in water, EtOH, MeOH, AcOH, DMSO, MeCN, THF; during heating in CH_2Cl_2, $CHCl_3$, CCl_4	[31]
4	$ArN_2{}^{+-}OTs$	1.371[4]	1.104	177.7	From –60 to –885.2 non-explosive	soluble in H_2O, EtOH, MeOH, AcOH, DMSO, MeCN, acetone	[21]
5	$ArN_2{}^{+}$ p-$C_{12}H_{25}C_6H_4SO_3{}^{-}$	Crystals cannot be grown for X-ray (oil)			From –118 to –410 non-explosive	Soluble in high and medium polarity solvents (water, DMSO, alcohols, ketones, acetic acid, chloroform) and non-polar (hexane, benzene, CCl_4) solvents	[29]
6	$ArN_2{}^{+-}OSO_2Camph$	1.41[5]	1.09	177	Stable and could be stored at room temperature under anhydrous conditions. No information about results of thermal analysis	Soluble in protic as well as aprotic solvents	[32]
7	$ArN_2{}^{+-}OSO_3{}^{-}SiO_2$	Crystals cannot be grown for X-ray			Stability was proved indirectly through the azo combination reaction after 6, 24, 48 and 72 hours. The diazotization and diazo coupling method was found to be safe and the grinding of these aryldiazonium salts was not found to be hazardous.	Insoluble in aqueous media	[34]
8	$ArN_2{}^{+-}N(SO_2)_2Ph$	1.387[6]	1.088	178.6	Stored at 0 ºC and at room temperature for two months underwent no decomposition	Soluble in water, HCO_2H, MeOH, DMSO, MeCN	[40]

Notes:

[1] Crystallographic info for Ph $N^{+}_{2}{}^{-}Cl$.

[2] Crystallographic info for $PhN^{+-}BF_4$.

[3] Crystallographic info for p-$IC_6H_4N_2{}^{+-}OTf$.

[4] Crystallographic info for p-$IC_6H_4N_2{}^{+-}OTs$.

[5] Crystallographic info for p-$BrC_6H_4N_2{}^{+-}OSO_2Camph$.

[6] Crystallographic info for 2,6-$ClC_6H_3N_2{}^{+-}N(SO_2)_2Ph$

The X-ray data show that the bond lengths N≡N are in the same range and differ not significantly. The length of the C-N bond is of interest from the point of view of predicting reactivity, since that participates in the process of *de-diazotization*. The length of this bond is higher in arenediazonium tetrafluoroborates, triflates and camphorasulfonates, which indicates their greater reactivity in contrast to diazonium salts.

C-N-N bond angle in diazonium sulfonate salts differs from the bond angle in classical diazonium salts by 1–3°, which may cause greater stability of these salts. At the C-N-N bond angle equal 180°, the salt forms an easily destroyed layered crystal lattice. Changing the bond angle leads to better coordination with the anion and the formation of more complex structure (Figure 21).

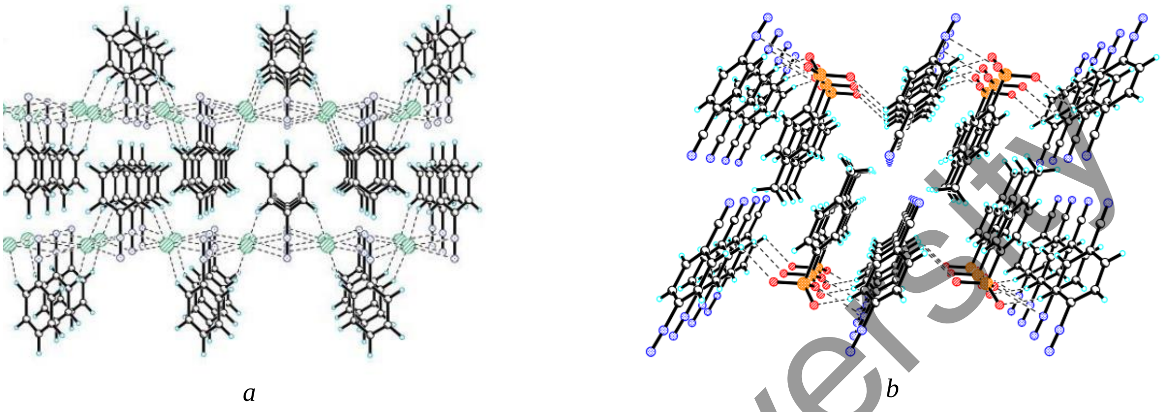


Figure 21. Crystalline networks of arenediazonium chloride (*a*) [48] and arenediazonium tosylate (*b*) [21]

The proof of stability for the diazonium salts was preserving chemical properties during the shelf life. Stability of arenediazonium silica-sulfate was proved indirectly through the azo combination reaction after 6, 24, 48, and 72 hours. Arenediazonium silica sulfates with electron-withdrawing groups on aromatic rings are more stable than those with electron-donating groups because of the instability of the resulting aryl cation. The diazotization and diazo coupling method was found to be safe and the grinding of these arenediazonium salts was not hazardous. At the same time, the authors of works recommend storing the obtained salts at 0 °C.

The stability of diazonium salts usually is compared by TGA-DSC methods. This method determines the temperature and energy of decomposition. According to the UNICEF international standard, the substance having decomposition energies of less than 800 kJ/mol is explosion-proof and can be transported. Among the considered salts, analysis was carried out only for arenediazonium tosylates, triflates, and dodecylbenzenesulfonates by TGA-DSC methods. All the studied salts are explosion-proof; the exception is *m*-nitro derivatives.

In work [49], for the first time, using isothermal flow calorimetry and DSC/TGA, authors determined the thermal decomposition energies of arenediazonium triflates, 4-nitrobenzene tosylate, and 4-nitrobenzentetrafluoroborate. The authors calculated the decomposition energies of salts accurately. 4-Nitrobenzenediazonium triflate of all the studied diazonium salts has increased stability stored under normal conditions. The experimental and theoretical results demonstrated that, compared to DSC/TGA, isothermal flow calorimetry more adequately reflected the energetics of the thermal decomposition of DSs and their storage stability under normal conditions.

Arenediazonium sulfonates have high solubility in water and in organic solvents, which opens up more areas for their usage in contrast to arenediazonium tetrafluoroborates and chlorides.

Conclusions

Arenediazonium sulfonates are easily synthesized by diazotization with sodium nitrite or alkyl nitrites in the presence of corresponding sulfonic acids with high yields. These diazonium salts have found wide application in the synthesis of aromatic azides, halides, triazenes, azo dyes, stilbenes, biaryls, etc. The structure of diazonium sulfonate salts corresponds to the structure of classical diazonium salts (chlorides, sulfates, tetrafluoroborates). A significant difference between arenediazonium sulfonates and other diazonium salts is their explosion safety and stability in an individual form. Arenediazonium tosylate, triflates, and camphorasulfonates are easily soluble both in water and in polar organic solvents. Arenediazonium dodecylbenzenesulfonates are dissolved in nonpolar organic media. These features of sulfonate salts are paramount for distinguishing characteristics of the effect of the acid anion on the stability, solubility, and reactivity of diazonium salts.

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Арендиазоний сульфонаттары: синтездеу, құрылымдық және физика-химиялық қасиеттерін салыстыру

Хош иісті диазоний тұздары органикалық синтезде маңызды құрылыс материалы болып табылады. Әр түрлі аниондары бар диазоний тұздарының көп мөлшері белгілі. Мақалада хош иісті диазоний сульфонаттары қарастырылған: тозилаттар, додецилбензолсульфонаттар, трифлаттар, камфорасульфонаттар, силикатсульфаттар. Мақаланың бірінші бөлімінде осы диазоний тұздарын синтездеу және қолдану туралы ақпарат берілген. Әдетте, диазоний тұздарын анилиндерді натрий нитритімен немесе алкил нитритімен тиісті сульфоқышқылдардың қатысуымен диазоттау арқылы оңай синтездеуге болады. Бұл диазоний тұздары хош иісті азидтер, галогендер, триазендер, азо-бояғыштары, стилбендер, биарилдер және т.б. синтездерінде кеңінен қолданылады. Жұмыстың екінші бөлімінде рентгендік талдау, инфрақызыл спектроскопия және термиялық талдау нәтижелерін салыстыру туралы ақпарат келтірілген. Диазонийдің сульфонат тұздарының құрылымы негізінен классикалық диазоний тұздарының (хлоридтер, сульфаттар, тетрафторбораттар) құрылымына сәйкес келеді. Сульфонаттардың арендиазонийі мен басқа диазоний тұздарының арасындағы маңызды айырмашылық олардың жарылыс қауіпсіздігі мен тұрақтылығы болып табылады. Арендиазоний тозилаттар, трифлаттар және камфорасульфонаттар суда да, полярлы органикалық еріткіштерде де оңай ериді. Арендиазоний додецилбензолсульфонаттары липофильді анионға байланысты полярлы емес органикалық ортада ериді. Арендиазоний сульфонат тұздарының бұл ерекшеліктері қышқыл анионының диазоний тұздарының тұрақтылығына, ерігіштігіне және реактивтілігіне әсер ету ерекшеліктерін түсіну үшін өте маңызды.

Кілт сөздер: диазоний тұздары, диазоттау, сульфонаттар, тозилаттар, трифлаттар, камфорасульфонаттар, силика-сульфаттар, додецилбензолсульфонаттар, рентген-құрылымдық талдау.

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Арендиазоний сульфонаты: синтез, сравнение структурных и физико-химических свойств

Ароматические соли диазония являются важными строительными блоками в органическом синтезе. Известно большое количество солей диазония с разными анионами-остатками. В данном обзоре рассмотрены ароматические диазоний сульфонаты: тозилаты, додецилбензолсульфонаты, трифлаты, камфорасульфонаты, силика-сульфаты. В первой части статьи представлены сведения по синтезу и применению данных солей диазония. Показано, что, как правило, указанные соли диазония легко синтезируются диазотированием анилинов нитритом натрия или алкилнитритами в присутствии соответствующих сульфокислот с высокими выходами. Данные соли диазония нашли широкое применение в синтезе ароматических азидов, галогенидов, триазенов, азокрасителей, стильбенов, биарилов и т.д. Аминопиридины диазотируются в присутствии сульфокислот с образованием других важных полупродуктов органического синтеза — пиридинилсульфонатов. Во второй части обзора дана информация по сравнению результатов рентгеноструктурного анализа, инфракрасной спектроскопии и термического анализа. Строение сульфонатных солей диазония в основном соответствует строению классических солей диазония (хлориды, сульфаты, тетрафторбораты). Существенным отличием арендиазоний сульфонатов от других солей диазония являются их взрывобезопасность и стабильность в индивидуальном виде. Арендиазоний тозилаты, трифлаты и камфорасульфонаты легко растворяются как в воде, так и в полярных органических растворителях. Арендиазоний додецилбензолсульфонаты, благодаря липофильному аниону, растворимы в неполярных органических средах. Эти особенности сульфонатных солей очень важны для понимания влияния аниона кислоты на устойчивость, растворимость и реакционную способность диазониевых солей.

Ключевые слова: соли диазония, диазотирование, сульфонаты, тозилаты, трифлаты, камфорасульфонаты, силика-сульфаты, додецилбензолсульфонаты, рентгеноструктурный анализ.

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