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SYNTHESIS, STRUCTURE AND CHEMICAL PROPERTIES OF 1-OXYDOPYRIDINEDIAZONIUM SULFONATES

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The products of diazotization of 2-, 3-, and 4-aminopyridin-1-oxides in the presence of TsOH, TfOH, and camphorsulfonic acid were investigated by IR, NMR, X-ray diffraction analysis, ESI/MS and MS2 spectroscopy, and B3LYP/aug-cc-pVDZ. The structures of the products and their stability during storage depend on the type of the starting aminopyridine. 4-Aminopyridin-1-oxide reacts to give stable diazonium sulfonates, and the 2-aminoisomer gives [1,2,3,5]oxotriazol[5,4-*a*]pyridinium-2 sulfonates. All products readily undergo reactions typical for diazonium salts. By the B3LYP/aug-cc-pVDZ method it was determined that 4-diazonium-pyridinium-1-oxide and benzoldiazonium cation have the highest stability in the series of diazonium cations of pyridine, pyridine-1-oxide and benzoldiazonium cation.

Keywords: aminopyridine-1-oxides, diazotization, 1-oxidopyridinediazonium sulfonates
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INTRODUCTION

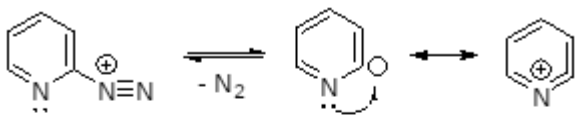
Aromatic and heteroaromatic diazonium salts are important building blocks of organic synthesis for the production of dyes, drugs and other useful products [1, 2], and are currently actively used to modify solid surfaces in the production of composite materials [2–4].

Unlike aromatic diazonium salts, pyridine diazonium compounds are less known and much less frequently used in organic synthesis. Under certain conditions, pyridine-3-diazonium tetrafluoroborate has been obtained in individual form; however, in the dry state, this salt is explosive [5]. Only 2 cases of diazotization of 4-aminopyridine in the presence of HBF_4 [6, 7] have been described, and it is reported that pyridine-4-diazonium tetrafluoroborate is an extremely unstable compound that rapidly decomposes in air. Examples of successful diazotization of 2-aminopyridine have not been found.

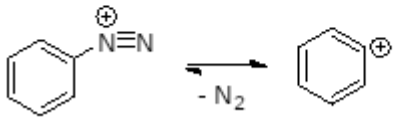
The aim of this work was to develop a method for the synthesis of 1-oxidopyridinediazonium sulfonates, and to conduct experimental and theoretical studies of the properties of this new class of diazonium compounds.

The difficulties in diazotizing aminopyridines are explained by the influence of the nitrogen atom in the cycle: in strongly acidic media, it is protonated, which deactivates the amino group (especially in positions 2 and 4 of the cycle) [8]. In weakly acidic media, diazotization occurs, but the resulting diazonium salt tends to lose the diazo group, especially in positions 2 and 4 of the cycle. According to quantum-chemical calculations M06–2X/6–311+G(d,p) [9], this is due to the increased thermodynamic stability of 2- and 4-pyridyl cations (I) formed as a result of dediazonization compared to the phenyl cation (II) (Scheme 1).

Scheme 1



I



II

Thus, pyridine diazonium salts approach the unstable diazonium compounds of the aliphatic series, the rapid decomposition of which is also determined by the relatively high stability of the resulting aliphatic carbocations.

The low stability of pyridinediazonium cations predetermines their increased reactivity, which is expressed, for example, in the easy substitution of the diazonium group with certain nucleophiles without initiation by copper salts. Examples of such useful transformations include simple and efficient diazotization-iodination of aminopyridines in the presence of TsOH and KI [10], formation of pyridyl sulfonates $PyOSO_2R$ as a result of diazotization under the action of TsOH, TfOH, camphorsulfonic acid [11-14]. Diazotization reactions of aminopyridines in acetonitrile or DMF lead to the formation of pyridine acetamides [15] and *N* , *N* -dimethylaminopyridines, respectively [16]. It has been shown [17] that aminopyridines are easily diazotized in hexafluoroisopropanol in the absence of strong acids, giving selectively and with high yields hexafluoroisopropyloxypyridines $PyOCH(CF_3)_2$. The same reaction with anilines proceeds non-selectively with the formation of product mixtures.

Thus, in some cases, the instability of pyridinediazonium cations can be used to obtain practically valuable compounds. However, in general, the instability of diazonium salts of pyridine structure is the main reason inhibiting the use of aminopyridines in diazonium transformations as widely as anilines.

RESULTS AND DISCUSSION

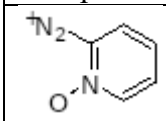
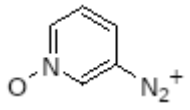
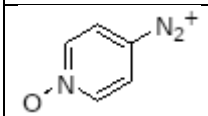
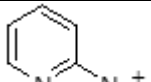
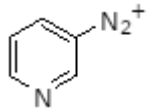
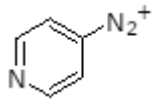
One of the ways to solve this problem may be the preliminary oxidation of aminopyridines to aminopyridine-1-oxides, the diazotization of which leads to poorly studied pyridinediazonium-1 oxides. Thus, only 1-hydroxypyridine-4-diazonium tetrafluoroborate has been obtained in individual form [18, 19], and only fragmentary information about its properties has been published [20]. It has been shown [21] that during the diazotization of all 3 isomeric aminopyridine-1-oxides in the presence of TsOH and KI, the diazonium salts formed *in situ* are converted to iodopyridine-1-oxides. However, the provided data do not allow to unambiguously determine the structure of pyridinediazonium-1-oxides, evaluate their stability, reactivity and possibilities for practical use.

We performed quantum-chemical DFT calculations using the B3LYP/aug-cc-VDZ method for diazonium cations of 3 isomeric pyridine-1-oxides (**1a–c**) in comparison with diazonium pyridines (**2a–c**) and benzenediazonium cation (**3**). All studied diazonium cations have a similar structure with linear arrangement of the diazonium group lying in the plane of the aromatic nuclei, which is typical for aromatic diazonium cations (for example, [9, 22]). Table 1 shows the bond lengths of C–N, N≡N and vibration frequencies of the diazonium group ν N≡N obtained as a result of optimization.

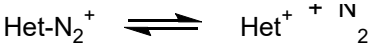
The N≡N bond lengths and vibration frequencies ν N≡N of cations **1a–c** , **2a–c** are typical for the diazonium group. The interatomic C–N distances in diazonium cations reflect the strength of the diazonium group binding to aromatic nuclei. The data presented in Table 1 indicates that the longest C–N distances are in pyridine diazonium cations **2a** and **2c** , which is consistent with the

instability of 2- and 4-pyridinediazonium salts, as mentioned above. At the same time, the shortest C–N distances are shown by diazonium cations **1a** and **1c** , in which the diazonium group is connected to the pyridine-1-oxide ring. These results indicate greater stability of diazonium salts with 1-oxidopyridine structure.

Table 1. Bond lengths (Å) and vibration frequencies of N≡N bonds in IR spectra of diazonium cations **1a–c** , **2a–c, 3,** calculated using the B3LYP/aug-cc-pVDZ method

Compound	C–N	N≡N	ν N≡N, cm $^{-1}$
 **1a**	1.363	1.116	2320.7
 **1b**	1.387	1.113	2348.0
 **1c**	1.363	1.119	2297.9
 **2a**	1.425	1.109	2370.6
 **2b**	1.379	1.114	2334.0
 **2c**	1.396	1.111	2365.6
PhN_2^+ **3**	1.382	1.114	2337.2

This is also indicated by comparative data on the thermodynamics of dediazonation reactions of diazonium cations **1a–c** , **2a–c, 3** (Table 2), calculated according to the equation (heteroaryl cations Het^+ were considered in the singlet state):



(1)

Overall, for the 3 types of diazonium cations studied, there is a correlation between the dediazoniation energies and the calculated C–N bond lengths (Table 1). The lowest heterolysis energies of pyridinediazonium cations **1a–c** , **2a–c** correspond to the longest C–N bonds, while the highest heterolysis energy of pyridinediazonium-1-oxides **1b** , **c** is associated with the shortest C–N bonds. An exception is cation **1a** , whose relatively low decomposition energy is determined by an abnormally low free energy due to stabilization of the positive charge by the adjacent oxygen atom (Scheme 2).

Scheme 2

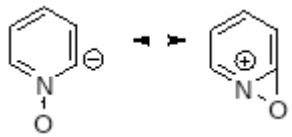
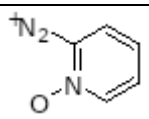
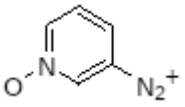
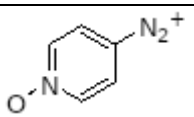
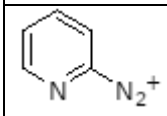
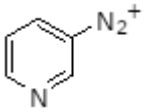
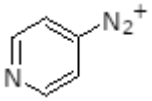


Table 2. Free energies (Δ *G*) of C–N bond cleavage in diazonium cations **1a–c** , **2a–c, 3** , calculated by the B3LYP/aug-cc-pVDZ method in the gas phase and in water (CPCM* approximation)

Compound	Δ *G* , kcal/mol	
	Gas phase	H_2O

 **1a**	15.10	15.98
 **1b**	19.96	21.99
 **1c**	35.95	31.36
 **2a**	–0.33	–1.85
 **2b**	13.99	15.12
 **2c**	10.85	11.66
PhN_2^+ **3**	19.74	17.95

* CPCM - Conductor-like Polarizable Continuum Model

The calculations predict enhanced stability of 1-oxidopyridinediazonium cations **1b** and **1c** not only in comparison with pyridinediazonium cations **2a–c** , but also with benzenediazonium cation **3** .

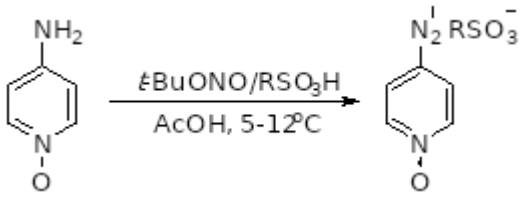
It is also important to note the different influence of the diazonium group position in the pyridine ring on the stability of diazonium cations in the series of isomeric pyridines and pyridine-1-oxides. Thus, for pyridine cations **2a–c** , an increase in stability is observed in the series **2a** < **2c** < **2b** . In contrast, pyridine-3-diazonium-1-oxide **1b** turns out to be the least stable, while pyridine-2-diazonium-1-oxide **1a** represents a special case, which will be discussed below.

The obtained theoretical data, along with earlier results [18, 19, 21], confirmed the feasibility of obtaining diazonium salts from aminopyridine-1-oxides. Diazonium sulfonates were chosen as the target diazonium salts from aminopyridine-1-oxides, since it was previously established that tosylates, triflates, and camphorsulfonates as counterions increase the stability of aromatic diazonium salts and also impart other positive properties (safety, good solubility) [23–26].

We showed that aminopyridine-1-oxides (**4–9**) undergo diazotization by the action of *tert* -butyl nitrite (*t* -BuONO) in acetic acid solution in the presence of such acids as TsOH, TfOH, and camphorsulfonic acid ($CamphSO_3H$) for 1 h at 5–12 °C with complete conversion. It was established that the nature of the resulting products and their properties strongly depend on the structure of the initial amines and sulfonic acids.

When diazotizing 4-aminopyridine-1-oxide **4** in the presence of TfOH and TsOH, stable crystalline compounds were isolated, identified by IR, NMR spectroscopy, and mass spectrometry as the previously unknown 1-oxidopyridine-4-diazonium triflate **4a** and tosylate **4b** with yields of 61 and 88%, respectively (Scheme 3).

Scheme 3



4 **4a,b**

RSO_3H = TfOH (**4a** , 61%), TsOH (**4b** , 88%)

The obtained diazonium salts **4a,b** can be stored in a dry state without changes for several weeks at 5–15 °C. Their true diazonium nature is confirmed by the absorption ν N≡N in the IR spectra at 2292 and 2264 cm^{-1} respectively. In the NMR ^{13}C spectra, a signal of the shielded *ipso* - carbon at the diazo group is registered in the 110 ppm region, which is a characteristic spectral criterion of well-studied arenediazonium sulfonates [23, 24].

Diazonium triflate **4a** is also detected in ESI/MS spectra in the form of cluster particles $(C_5H_4NON_2^+)_n TfO^{n-1}{}_{n-1}$, consisting of (n+1) diazonium cations and n-anions (TfO^-) (Fig. 1). Similar clusters have been previously observed for arenediazonium triflates [25]. The main fragmentation pathway of the 1-oxidopyridine-4-diazonium cation **1c** is the elimination of molecular nitrogen with the formation of the $C_5H_4NO^+$ cation.

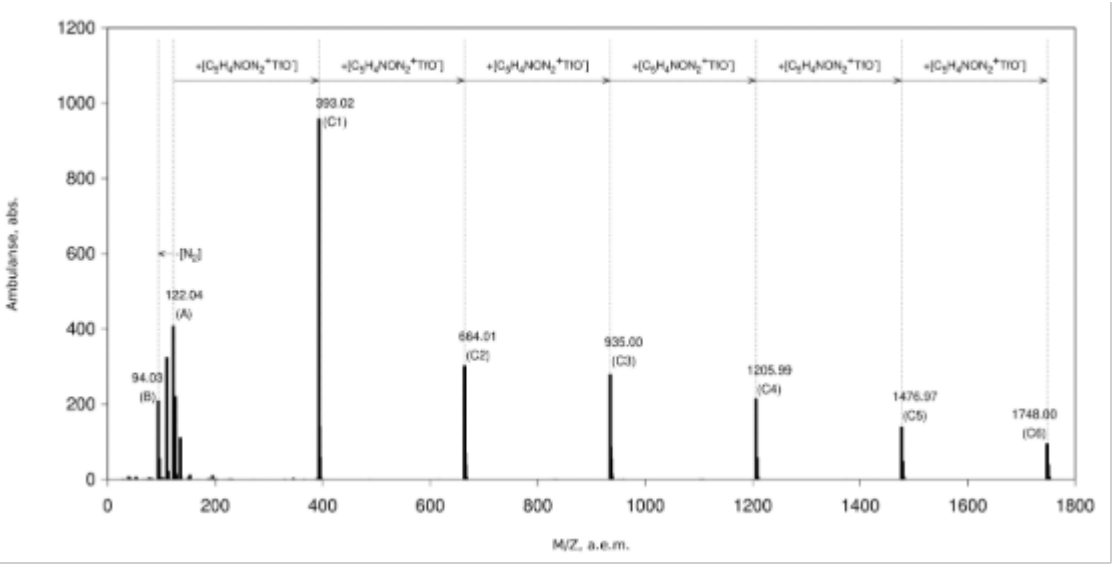


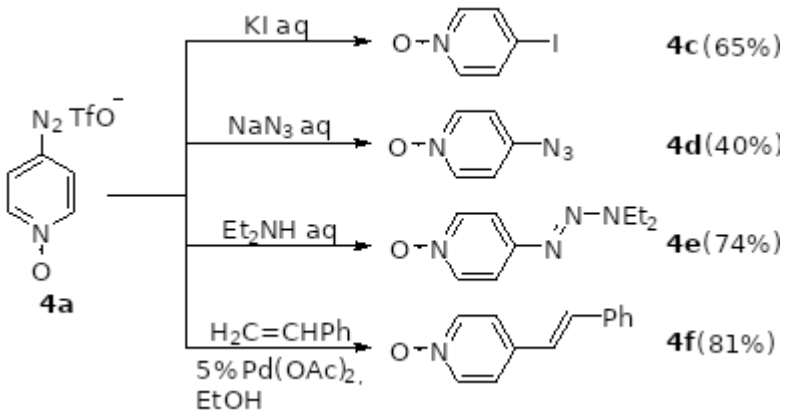
Fig. 1. ESI/MS spectrum of C_5H_4NO-4-$N_2^+ TfO$ [4a] **4a** in positive ionization mode. A = $[C_5H_4NON_2^+]$, *m/z* = 122.04; B = $[C_5H_4NO^+]$, *m/z* = 94.03; cluster cations Cn = $[C_5H_4NON_2^+]_{n+1}[TfO^-]_n$. *m/z* for cations C1...C6 = 393.02; 664.1; 935.00; 1205.99; 1476.97; 1747.96.

Thus, in accordance with the above quantum chemical calculations, diazonium salts **4a,b** prove to be sufficiently stable compounds, similar in this respect to arenediazonium sulfonates. In the case of using camphorsulfonic acid, we were unable to isolate individual products, although diazotization proceeds with complete conversion, the reaction mixtures give a positive test with 2-naphthol, and absorption at 2300 cm^{-1} is observed in the IR spectra.

The chemical properties of diazonium sulfonates **4a,b** were similar to those of stable arenediazonium sulfonates. They readily react with KI, NaN_3 , diethylamine, and also undergo cross-coupling reaction with styrene in the presence of $Pd(OAc)_2$, forming the corresponding substituted 1-hydroxypyridines **4c–f** (Scheme 4).

1-Hydroxypyridine-4-diazonium tosylate **4b** undergoes the same reactions as triflate **4a** , and shows no differences in reactivity.

Scheme 4



Unlike 4-aminopyridine-1-oxide **4** diazotization of 3-amino derivative **5** in the presence of TfOH, TsOH and CamphSO $_3$H proceeds with the formation of compounds that rapidly decompose in air, which could not be isolated in pure form. However, the diazonium nature of these products was confirmed by a positive test with 2-naphthol, IR absorption ν N≡N 2302 cm $^{-1}$ (TfO $^-$) and 2316 cm $^{-1}$ (TsO $^-$), as well as previously obtained results on diazotization-iodination of 3-aminopyridine-1 oxide **5** [21]. Thus, the experimentally observed instability of diazotization products of 3-aminopyridine-1-oxide **5** fully confirms the calculated data (Tables 1, 2), demonstrating the weak bond of the diazonium group in position 3 with the 1-oxypyridine cycle.

When diazotizing 2-aminopyridine-1-oxide **6** and its 6-methyl-substituted **7** in the presence of TfOH (Scheme 5, Table 3) under the conditions specified above, stable products were isolated that gave a positive test with 2-naphthol and were completely converted to 2-iodopyridine-1-oxide and 2-azidopyridine-1-oxide in reactions with KI and NaN $_3$ (see below). However, the IR spectra of these products lacked absorption bands in the region of 2200–2300 cm $^{-1}$,characteristic of the N≡N group.

A single crystal of the diazotization product of 2-amino-6-methylpyridine-1-oxide **7** was studied by X-ray diffraction analysis (XRD). The obtained data indicate that the reaction product is not a diazonium salt, but 5-methyl[1,2,3,5]oxotriazole[5,4a *a*]pyridinium-2 triflate **7a** (Fig. 2, Scheme 5, Table 3).

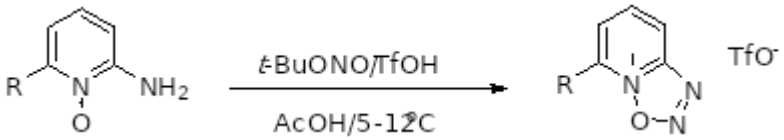
a *b*

Fig. 2. Structure of 5-methyl [1,2,3,5]oxotriazole[5,4a *a*]pyridinium -2 triflate **7a** according to XRD data: (*a*) asymmetric unit of the crystal structure, hydrogen atoms are not shown; (*b*) intermolecular interactions in packing, view along the *b* axis.

Compound **7a** crystallizes in the monoclinic system, space group $P\,2_1/c$. The asymmetric unit includes one [1,2,3,5]oxotriazole[5,4a *a*]pyridinium cation and one triflate ion (Fig. 2, *a*). When ions are packed in the crystal lattice, intermolecular interactions appear between them in the form of short contacts between oxygen atoms of triflate ions and nitrogen and carbon atoms of the heterocyclic cation with an average O···N and O···C distance of 2.94 Å, as well as with hydrogen atoms of the methyl group and aromatic ring (O···H distance 2.38 Å) (Fig. 2, *b*). These intermolecular interactions connect the ions into supramolecular layers located parallel to the crystallographic plane *bc* . The layers are connected through F···F contacts between triflate ions

(Fig. 2, *b*). The internuclear F···F distance is 2.726 Å, which is 0.214 Å less than the sum of the van der Waals radii of fluorine atoms and is the shortest according to available data on contacts of this type between triflate ions [26, 27]. It should also be noted that the obtained crystal structure is the first example of a structurally characterized compound with a [1,2,3,5]oxotriazole[5,4a *a*]pyridine heterocycle.

Scheme 5



6, 7 R = H (**6a**), 6-Me (**7a**)

Previously, [1,2,3,5]oxotriazole[5,4a *a*]pyridinium-2 tetrafluoroborate was obtained with a yield of 78% by diazotization of 2-aminopyridine-1-oxide **6** in the presence of HBF_4 [18], but its structure was determined only by indirect methods.

Using 2-aminopyridine-1-oxide **6** as an example, it was shown that diazotization in the presence of other sulfonic acids (TsOH, $CamphSO_3H$) also leads to the formation of diazonium salts with oxotriazolpyridinium structure **6b** , **c** respectively (Table 3).

Thus, the formation of cyclic compounds with oxotriazolpyridinium structure is a common characteristic of the diazotization processes of 2-aminopyridine-1-oxides. These compounds can be classified as intramolecular "diazotates" ArN=NOR, which are obtained from aromatic diazonium salts and hydroxyl-containing compounds usually at elevated pH values [28]. It can be assumed that in the initially formed diazonium cation **1a'** the diazonium group enters into the same reaction with the nucleophilic oxygen of the N→O group (Scheme 6). To understand the reasons for these transformations, we determined the free energy difference between the [1,2,3,5]oxotriazol[5,4a *a* pyridinium-2 cation **1a** and cation **1a'** using the B3LYP/aug-cc-pVDZ method (Scheme 6).

Scheme 6

1a' **1a**

ΔG 0 kcal/mol –3.5 kcal/mol (–2.3 kcal/mol in H_2O using CPCM approximation)

The calculation results indicate that cation **1a** is the thermodynamically more stable form of the diazonium cation **1a'** . As the polarity of the medium increases, the free energy difference between the isoelectronic forms **1a'** and **1a** decreases due to the greater polarity of the diazonium cation **1a'** .

The MS2 spectra of compounds **6a–c** (Fig. 3) indicate that their fragmentation proceeds differently than for true diazonium salts **4a,b** . In this case, not N_2 is cleaved, but N_2O, i.e., the simultaneous loss of the nitrogen atoms of the diazonium group and the oxygen atom of the N→O group. There are no lines corresponding to the separate loss of oxygen or molecular nitrogen, which indicates the presence of a strong intramolecular N–O–N=N– interaction and further confirms the pyridinooxotriazole structure of these compounds.

Given the insignificant difference in free energies between the diazonium cation **1a** and cation **1a'** (Scheme 6), it seems likely that substituents in the ring of 2-aminopyridine-1-oxide **6** can affect the ratio of the 2 forms of diazotization products.

As noted above, the 6-methyl derivative (**7**) selectively forms only the corresponding cyclic form **7a** . It was shown that the diazotization products of 2-amino-5-chloropyridine-1-oxide (

8) and 2-amino-5-bromopyridine-1-oxide (**9**) represent mixtures of cyclic (**8a** , **9a**) and linear (**8b** , **9b**) isomers (Table 3).

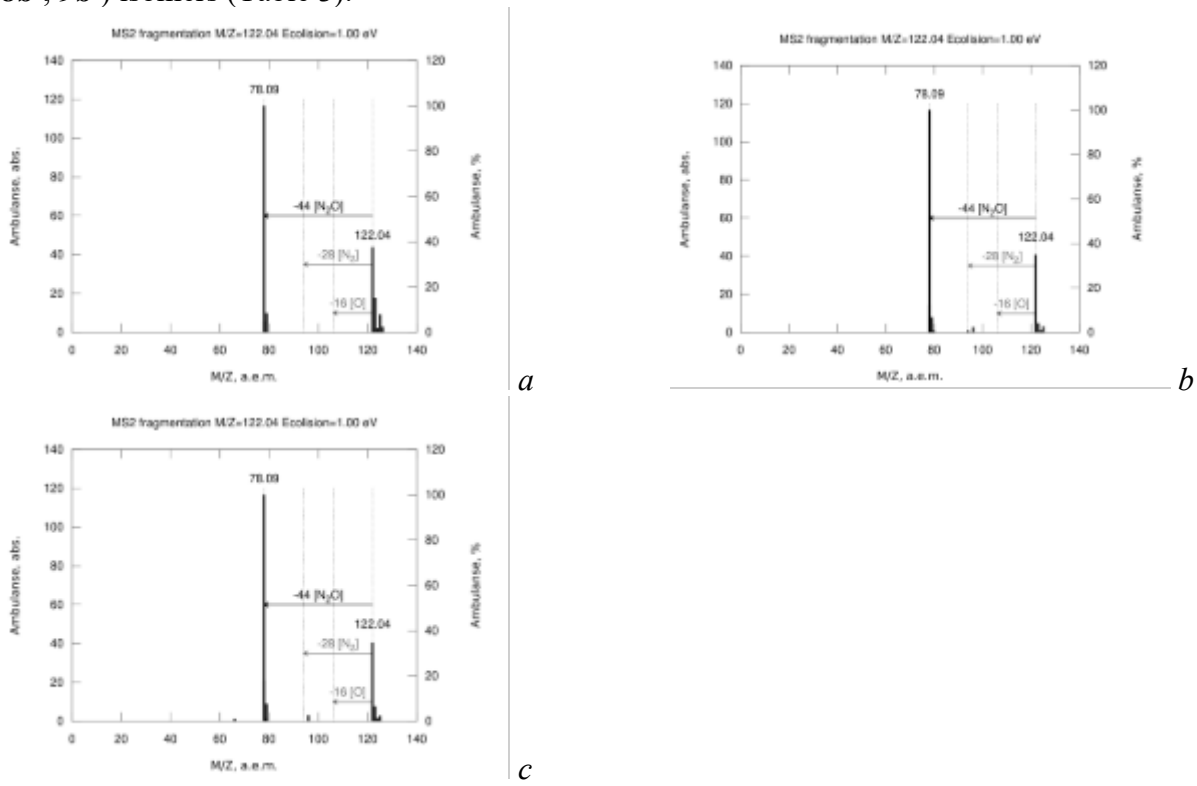
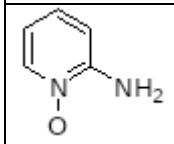
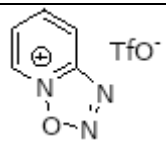
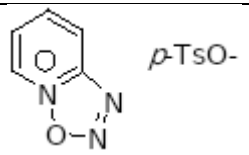
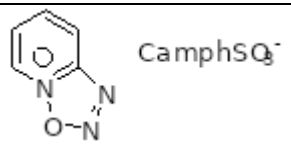
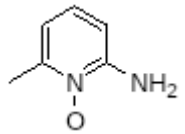
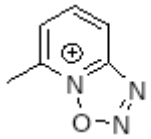
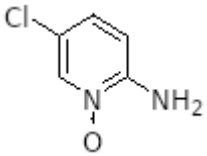
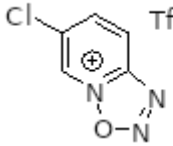
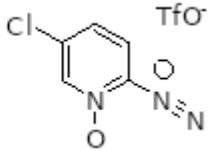
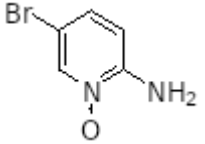
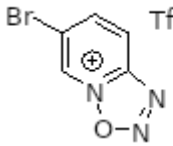
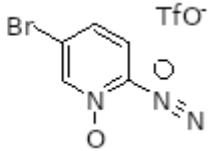


Fig. 3. MS2 spectrum of pyridinium cation **1a** (122.04 *m/z*) for salts: *a*) C_5H_4NO - 2 - N_2^+ TfO ((**6a**), *b*) C_5H_4NO - 2 - N_2^+ TsO ((**6b**), *c*) C_5H_4NO - 2 - N_2^+ $CamphSO_3$ ((**6c**).

According to NMR ^1H spectra, the ratio of cyclic to linear forms is 2:1. The presence of true diazonium salts in these products is also confirmed by the absorption ν N≡N in IR spectra at 2275 cm^{-1} (**8b**) and 2272 cm^{-1} (**9b**). Calculations by the B3LYP/aug-cc-pVDZ method for both forms **8a** and **8b** showed that Δ *G* between them is -1.44 kcal/mol, which is significantly less than for forms **1a** and **1a'** (Scheme 4), and in polar H_2O their free energies are practically the same. Overall, the calculations performed are consistent with experiments and explain the peculiarities of diazotization of 2-aminopyridine-1-oxides.

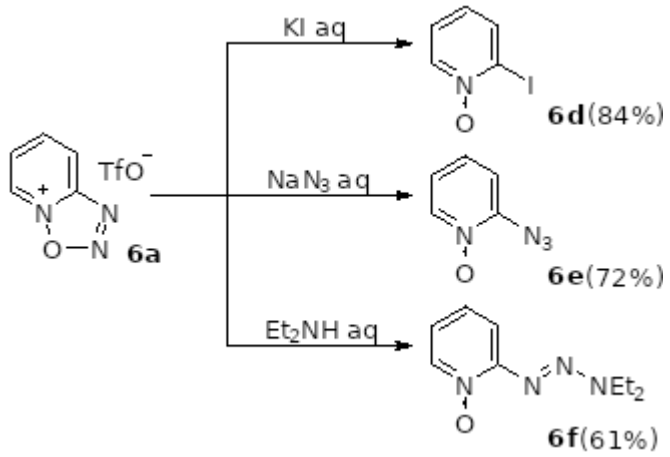
All obtained salts **6a-c, 7a, 8a,b, 9a,b** are highly soluble in both water and organic polar and moderately polar solvents (AcOH, DMSO, DMF, MeCN, EtOH, CH_2Cl_2, $CHCl_3$, THF).

Table 3. Diazotization of 2-aminopyridine-1-oxides **6** – **9** using *t* -BuONO in AcOH (5–12 °C, 1–2 h)

Substrate	Acid	Product	Yield, %
 **6**	TfOH	 **6a**	78
	TsOH	 **6b**	94
	$CamphSO_3H$	 **6c**	96
 **7**	TfOH	 **7a**	80
 **8**	TfOH	 **8a** +  **8b**	54
 **9**	TfOH	 **9a** +  **9b**	70

Using the example of 1-oxidopyridine-2-diazonium triflate **6a** its high reactivity toward KI, NaN_3 and Et_2NH was demonstrated, forming products **6d–f** with preservation of the *N* -oxide group of the pyridine skeleton (Scheme 7).

Scheme 7



Tosylate **6b** and camphorsulfonate **6c** provide essentially the same results in these reactions, i.e., the influence of the anion on reactivity is not observed to any significant degree.

The reactions with nucleophiles shown in Scheme 7 are typical for aromatic diazonium salts. Given the proximity of free energies of the pyridinium cation **1a** and diazonium cation **1a'** (Scheme 4), it cannot be excluded that these reactions proceed with the participation of diazonium cation **1a'** , which is in equilibrium with the cyclic oxotriazole form **1a** . From a practical point of view, this does not play a significant role and demonstrates the potential of using 2-aminopyridine-1-oxides in synthesis in diazotization reactions.

EXPERIMENTAL SECTION

All starting aminopyridines from Sigma-Aldrich were used without additional purification. *N* -Oxides of aminoheterocycles **4–9** were obtained according to the procedure from the literature [29]. The progress and completion of reactions were monitored using GC-MS and TLC on Sorbfil PTSC-AF-A-UV plates. Spots were detected using a UV lamp with a wavelength of 254 nm. Chromatography-mass spectra were recorded on an Agilent Technologies 7890A GC System (USA) with an Agilent 5975C mass-selective detector (70 eV), carrier gas - helium, HP-5MS UI column (30 m × 0.25 mm), 1–3 min: 70°C, 3–17 min: 70–280°C (15ºC/min), 17–22 min: 280°C. NMR spectra ^{1}H and ^{13}C were recorded on a Bruker AVANCE III HD instrument (Germany) (operating frequency ^{1}H – 400 MHz, ^{13}C – 100 MHz). Melting points of the obtained compounds were determined using a METTLER TOLEDO MP 50 instrument (Switzerland). Elemental analysis was performed on an elemental analyzer from EuroEA (Italy), model EA3000, with the Calidus 2E3 results processing program and a high-resolution mass spectrometer with electrospray ionization. IR spectra were recorded on an Agilent Cary 630 FTIR spectrometer (USA) in solid samples and solutions (range 800–4000 cm^{-1}). LC-HRMS mass spectra (ESI, APCI) were recorded on an Agilent Infinity chromatograph with an AccurateMass QTOF 6530 mass detector (USA). X-ray diffraction data for single crystals of compound **7a** were recorded at 150 K on a Bruker D8 Venture diffractometer (Germany) with a CMOS PHOTON III detector and a Mo-IμS 3.0 microfocus source, MoKα radiation, λ = 0.71073 Å. Data processing was performed using the APEX 3 package. Crystal structures were solved using the SHELXT

package [30] and refined by full-matrix least squares method in anisotropic (except for hydrogen atoms) approximation using the SHELXL package [31].

1-Oxidopyridinediazonium sulfonates 4a,b, 6a–c, 7a, 8a,b, 9a,b. *General procedure.* To a solution of aminopyridine-1-oxides **6–9** (2 mmol) in 5 ml of glacial acetic acid, the corresponding sulfonic acid (3 mmol) was added, cooled to 5 °C and *tert* -butyl nitrite 0.36 ml (3 mmol) was added dropwise with intensive stirring. The reaction mixture was kept at 5 °C for 40 min. The progress of the reaction was monitored by TLC (eluent CH_2Cl_2-EtOH, 9:1) and qualitative reaction with 2-naphthol. Then diethyl ether (100 ml) was added to the reaction mixture and left for 1 day at –20°C. The precipitated diazonium salt was filtered off, washed on the filter with cold Et_2O (4×15 ml), dried under vacuum. If necessary, additional purification of the reaction product was carried out by reprecipitation from acetic acid solution with diethyl ether.

1-Oxidopyridine-4-diazonium triflate (4a). Yield 0.33 g (61%). White crystals. $T_{decomp.}$ = 124–126°C. IR spectrum, ν, cm-1: 3120–3032 m (CH), 2264 s (N≡N), 1300 s (N-O). NMR spectrum ^{1}H (400 MHz, DMSOd d_6): δ, ppm: 8.65-8.70 m ($4H_{arom}$). NMR spectrum ^{13}C (100 MHz, DMSOd d_6): δ, ppm: 107.8, 115.9–125.5 q (J 320 Hz), 129.5, 142.3. High-resolution mass spectrum with electrospray ionization: cation – *m/z* $[M]^+$ calculated for $C_5H_4N_3O^+$: 122.0349, found 122.0360; adduct – *m/z* $[M]^+$ calculated for $(C_5H_4N_3O)_2^+(CF_3O_3S)^-$ 393.0223; found 393.0208.

1-Oxidopyridine-4-diazonium *p* -toluenesulfonate (4b). Yield 0.52 g (88%). White crystals. Tm_m = 128–129°C. IR spectrum, ν, cm-1: 3081–3023 m (CH), 2292 s (N≡N), 1313 s (N–O). NMR spectrum ^{1}H (400 MHz, DMSO-d d_6), δ, ppm: 2.28 s (3H, CH), 7.11 d ($2H_{arom}$, J 8 Hz), 7.48 d ($2H_{arom}$, J 8 Hz), 8.69 s ($4H_{arom}$). NMR spectrum ^{13}C (100 MHz, DMSO-d d_6), δ, ppm: 20.9, 108.0, 125.5, 128.2, 129.5, 137.9, 142.2, 145.4 High-resolution mass spectrum with electrospray ionization: *m/z* $[M]^+$ calculated for $C_5H_4N_3O$: 122.0349, found 122.0360; adduct – *m/z* $[M]^+$ calculated for $(C_5H_4N_3O)_2^+(C_7H_7O_3S)^-$ 415.0819; found 415.0816.

1-Oxidopyridine-2-diazonium triflate (6a). Yield 0.423 g (78%). White crystals. T_m = 86–88°C. IR spectrum, ν, cm^{-1}: 3081–3043 m (CH). NMR spectrum ^{1}H (400 MHz, DMSO-d d_6), δ, ppm: 8.65–8.69 m ($1H_{arom}$), 8.83-8.87 m ($1H_{arom}$), 9.37 d ($1H_{arom}$, J 8.6 Hz), 10.22 d ($1H_{arom}$, J 6.6 Hz). NMR spectrum ^{13}C (100 MHz, DMSO-d d_6), δ, ppm: 115.9–125.5 q (J 320 Hz), 131.1, 132, 142.1, 142.8. High-resolution mass spectrum with electrospray ionization: *m/z* $[M]^+$ calculated for $C_5H_4N_3O^+$: 122.0349; found 122.0364; adduct – *m/z* $[M]^+$ calculated for $(C_5H_4N_3O)_2^+(CF_3O_3S)^-$ 393.0223; found 393.0236.

1-Oxidopyridine-2-diazonium *p* -toluenesulfonate (6b). Yield 0.55 g (94%). Light brown crystals. Mp = 117–119°C. IR spectrum, ν, cm^{-1}: 3318–3120 m (CH). NMR spectrum ^{1}H (400 MHz, D_2O), δ, ppm: 2.25 s (3H, CH), 7.21 s (2H), 7.50 s (2H, CH_{arom}), 8.46 s ($1H_{arom}$), 8.76 s (1H), 9.82 s ($1H_{arom}$), 9.00 s ($1H_{arom}$). NMR spectrum ^{13}C (100 MHz, DMSO-d d_6), δ, ppm: 20.8, 124.8, 125.5, 128.2, 131.1, 137.9, 141.9, 142.6, 145.4. High-resolution mass spectrum with electrospray ionization: *m/z* $[M]^+$ calculated for $C_5H_4N_3O$: 122.0349, found 122.0365; adduct – *m/z* $[M]^+$ calculated for $(C_5H_4N_3O)_2^+(C_7H_7O_3S)^-$ 415.0819; found 415.0829.

1-Oxidopyridine-2-diazonium camphorsulfonate (6c). Yield 0.67 g (96%). White crystals. Mp = 118–120°C. IR spectrum, ν, cm^{-1}: 3084–3025 m (CH). NMR spectrum ^{1}H (400 MHz, DMSOd d_6), δ, ppm: 0.73 s (3H, CH), 1.03 s (3H, CH), 1.27 d (2H, J 8.7 Hz), 1.77–1.94 m (3H), 2.21–2.26 m (1H), 2.38 d (1H, J 14.7 Hz), 2.61–2.66 m (1H), 2.86 d (1H, J 14.7 Hz), 6.84–6.87 m ($1H_{arom}$), 7.15 d (1H, J 8.7 Hz), 7.78–7.82 m ($1H_{arom}$), 8.24–8.29 m ($1H_{arom}$), 8.66–8.70 m ($1H_{arom(triazole)}$), 8.84–8.88 m ($1H_{arom(triazole)}$), 9.39 d ($1H_{arom(triazole)}$, J 8 Hz), 10.24 d ($1H_{arom(triazole)}$, J 6.6 Hz). NMR spectrum ^{13}C (100 MHz, DMSOd d_6), δ, ppm: 19.6, 20.1,

24.2, 26.4, 42.1, 46.8, 47.2, 58.2, 124.8, 131.2, 132.1, 142, 142.7, 216.2. High-resolution mass spectrum with electrospray ionization: *m/z* $[M]^+$ calculated for $C_5H_4N_3O$: 122.0349, found 122.0370; adduct – *m/z* $[M]^+$ calculated for $(C_5H_4N_3O)_2^+(C_{10}H_{15}O_4S)^-$ 475.1394, found 475.1389.

6-Methyl-1-oxidopyridine-2-diazonium triflate (7a). Yield 0.456 g (80%). White crystals. Mp_m = 96–98°C. IR spectrum, ν, cm^{-1}: 3079–3000 br (CH). NMR spectrum ^1H (400 MHz, DMSOd d_6), δ, ppm: 3.03 s (3H, CH), 8.61 d (1H, *J* 7.6 Hz), 8.83–8.87 m (1H), 9.27 d (1H, *J* 8.3 Hz). NMR spectrum ^{13}C (100 MHz, DMSOd d_6), δ, ppm: 16.7, 115.8–125.4 q (*J* 320 Hz), 121.8, 130.7, 143.1, 143.4, 143.5. High-resolution mass spectrum with electrospray ionization: *m/z* $[M]^+$ calculated for $C_6H_6N_3O$: 136.0505, found 136.0505; adduct – *m/z* $[M]^+$ calculated for $(C_6H_6N_3O)_2^+(CF_3O_3S)^-$ 421.0536, found 421.0511. Crystallographic data of compound **7a** : $(C_6H_6N_3O)(CF_3SO_3)$, *M* 258.21 g/mol, monoclinic system, space group $P2_1/c$, *a* = 11.378(3) Å, *b* = 6.9013(17) Å, *c* = 18.769(2) Å, β = 97.956(8)°, *V* = 1128.3(5) $Å^3$, *Z* = 4, *T* = 150(2) K, μ = 0.34 mm^{-1}, d_{calc} = 1.679 g/cm^3, 14858 measured reflections, 1989 independent reflections (R_{int} = 0.075), goodness of fit on F^2 1.107, *R* - factors with I > 2σ(I): R_1 0.0886, w R_2 0.167; *R* - factors for all data: R_1 0.0648, w R_2 0.182. Complete tables of interatomic distances and valence angles, atomic coordinates, and atomic displacement parameters have been deposited in the Cambridge Structural Database under the number CCDC 2324250 and can be requested at www.ccdc.cam.ac.uk/data_request/cif, and can also be obtained from the authors.

5-Chloro-1-oxidopyridin-2-diazonium triflate (mixture of compounds 8a, 8b). Yield 0.33 g (54%). Yellow crystals. $M.p._{pl}$ = 91–92°C. IR spectrum, ν, cm^{-1}: 3102–3060 m (CH), 2275 s (N≡N), 1393 s (N–O). NMR spectrum ^1H (400 MHz, DMSO-d d_6), δ, ppm: 7.67–7.69 m (2H, CH_{arom}), 7.79–7.81 m (1H, CH_{arom}), 8.06 d (2H, $CH_{arom(triazole)}$, *J* 8.8 Hz), 8.21 d (2H, $CH_{arom(triazole)}$, *J* 8.8 Hz), 8.74 s (1H, CH_{arom}), 9.19 s (2H, CH_{arom}). NMR spectrum ^{13}C (100 MHz, DMSO-d d_6), δ, ppm: 116.0–125.6 q (*J* 320 Hz), 123.4 (CH_{arom}), 127.5 (CH_{arom}), 128.7 ($CH_{arom(triazole)}$), 129.9 ($CH_{arom(triazole)}$), 134.0 (CCl_{arom}), 137.9 ($CN_{arom(triazole)}$), 138.7 (CH_{arom}), 140.1 ($CCl_{arom(triazole)}$), 140.7 ($CH_{arom(triazole)}$), 153.8 ($CN_{2\,arom}$). High resolution mass spectrum with electrospray ionization: *m/z* $[M]^+$ calculated for $C_5H_3ClN_3O$: 155.9959, found 155.9975; adduct – *m/z* $[M]^+$ calculated for $(C_5H_3ClN_3O)_2^+(CF_3O_3S)^-$ 460.9444, found 460.9450.

5-Bromo-1-oxidopyridin-2-diazonium triflate (mixture of compounds 9a, 9b). Yield 0.49 g (70%). Yellow crystals. $Melting_{point}$ = 115–117°C. IR spectrum, ν, cm^{-1}: 3100–3068 m (CH), 2272 s (N≡N), 1391 s (N–O). NMR spectrum ^1H (400 MHz, DMSO-d d_6), δ, ppm: 7.62 d (1H, CH_{arom}, *J* 8.4 Hz), 7.92 d (1H, CH_{arom}, *J* 8.4 Hz), 8.12 d (1H, $CH_{arom(triazole)}$, *J* 8.8 Hz), 8.18 d (1H, $CH_{arom(triazole)}$, *J* 8.8 Hz), 8.81 s (1H, CH_{arom}), 9.27 s (1H, $CH_{arom(triazole)}$). NMR spectrum ^{13}C (100 MHz, DMSO-d d_6), δ, ppm: 116.0–125.6 q (*J* 320 Hz), 123.4 (CH_{arom}), 121.8 (CBr_{arom}), 123.5 ($CH_{arom(triazole)}$), 128.6 ($CBr_{arom(triazole)}$), 129.7 ($CH_{arom(triazole}$), 130.1 (CH_{arom}), 131.3 ($CH_{arom(triazole)}$), 138.2 ($CN_{arom(triazole)}$), 140.5 (CH_{arom}), 142.5 ($CH_{arom(triazole}$), 154.1 ($CN2_{arom}$). High-resolution mass spectrum with electrospray ionization: *m/z* $[M]^+$ calculated for $C_5H_3BrN_3O$: 199.9454, found 199.9456; adduct – *m/z* $[M]^+$ calculated for $(C_5H_3BrN_3O)_2^+(CF_3O_3S)^-$ 548.8434, found 548.8445.

Iodopyridine-1-oxides 4c, 6d. *General procedure.* To a solution of KI 0.216 g (1.3 mmol) in 5 ml of water, cooled to 10–15°C, pyridine-1-oxide diazonium sulfonate **4a** or **6a** 0.271 g (1 mmol) was added in portions with stirring. Stirring was continued for 20–30 min. The end of the reaction was determined by a negative test with 2-naphthol. The pH of the solution was adjusted to 8.0–9.0 with 10% K_2CO_3 solution. The released iodine was reduced with 20% Na_2SO_3 solution. The mixture was extracted with dichloromethane 4 × 25 ml. The combined organic

layer was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The product was purified by flash chromatography (eluent CH_2Cl_2–MeOH, 9:1).

4-Iodopyridine-1-oxide (4c) C_5H_4INO. Yield 0.144 g (65%). White crystals. M_p = 169–170 °C (170–171°C [21]).

2-Iodopyridine-1-oxide (6d) C_5H_4INO. Yield 0.186 g (84%). Light brown crystals. M_p = 121–122 °C (119–121°C [21]).

Azidopyridine-1-oxides 4d, 6e. *General procedure.* To a solution of NaN_3 0.085 g (1.3 mmol) in 5 ml of water, cooled to 10–15°C, pyridine-1-oxide diazonium sulfonate **4a** or **6a** 0.271 g (1 mmol) was added in portions with stirring. Stirring was continued under cooling for 20 min. The end of the reaction was determined by a negative test with 2-naphthol. The pH of the solution was adjusted to 8.0–9.0 with 10% K_2CO_3 solution. The mixture was extracted with dichloromethane 4 × 25 ml. The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The product was purified by column chromatography (eluent hexane–ethyl acetate, 8:1).

4-Azidopyridine-1-oxide (4d) $C_5H_4N_4O$. Yield 0.054 g (40%). White crystals. M_p = 138–139 °C (140°C [32]).

2-Azidopyridine-1-oxide (6e) $C_5H_4N_4O$. Yield 0.98 g (72%). White crystals. $M.p._{pl}$ = 86–88 °C (83.5–84.5°C [33]). NMR ^1H spectrum (400 MHz, $CDCl_3$), δ, ppm: 6.96 d.d (1H, CH_{arom}, J_1 8 Hz, J_2 2 Hz), 7.06–7.1 m (1H, CH_{arom},), 7.24–7.28 m (1H, CH_{arom}), 8.17 d.d (1H, CH_{arom}, J_1 6.4 Hz, J_2 1.6 Hz). NMR ^{13}C spectrum (100 MHz, $CDCl_3$), δ, ppm: 117.0, 120.7, 127.3, 139.2, 144.2.

4-Styrylpyridine-1-oxide (4f) $C_{13}H_{11}NO$. To a solution of 1-oxidopyridine-4-diazonium *p* -toluenesulfonate **(4b)** 0.293 g (1 mmol) in 5 ml EtOH, styrene 0.173 ml (1.5 mmol) and $Pd(OAc)_2$ 0.011 g (5 mol%) were added. The reaction mixture was stirred at 70°C. The completion of the reaction was determined by a negative test with 2-naphthol. The solvent was evaporated under vacuum. The product was purified by column chromatography (eluent CH_2Cl_2 –EtOH, 9:1). Yield 0.16 g (81%). White crystals. $M.p._{pl}$ = 165–166°C. (167–169 [34]). NMR ^1H spectrum (400 MHz, DMSOd d_6), δ, ppm: 7.24 d (1H, *J* 16.5 Hz), 7.28–7.36 m (1H), 7.37–7.43 m (3H), 7.61 d (4H, *J* 7.1 Hz), 8.19 d (1H, *J* 6.7 Hz). NMR ^{13}C spectrum (100 MHz, DMSOd d_6), δ, ppm: 123.5, 124.6, 126.9, 128.4, 128.9, 131.5, 134.1, 136.4, 138.7.

Pyridyltriazenes 4e, 6f. *General procedure.* To a solution of diazonium salt **4** a or **6a** 0.54 g (2 mmol) in 10 ml of water, cooled to 5°C, a solution of diethylamine 0.41 ml (4 mmol) in 10 ml of water was added dropwise. Then the reaction mass was stirred at room temperature for 1-2 h. The end of the reaction was determined by a negative test with 2-naphthol, as well as by TLC (eluent CH_2Cl_2-EtOH, 9:1). Extraction was performed with dichloromethane (3 × 15 ml), the combined organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum. The product was purified by flash chromatography (eluent CH_2Cl_2-EtOH, 9:1).

4-(3,3-Diethyltriaz-1-en-1-yl)pyridine-1-oxide (4e) . Yield 0.29 g (74%), yellow crystals, $m.p._{pl}$ 107-108°C. IR spectrum, ν, cm^{-1} : 3097-2871 br (CH), 1465 ($\delta_s CH_2$), 1377 ($\delta_s CH_3$). NMR ^1H spectrum (400 MHz, $CDCl_3$), δ, ppm: 1.2-1.23 m (3H, CH_3), 1.32-1.36 m (3H, CH_3), 3.77-3.83 m (4H, CH_2), 7.28-7.3 m (2H, CH_{arom}), 8.48 d (2H, CH_{arom}, *J* 6 Hz). NMR ^{13}C spectrum (100 MHz, $CDCl_3$), δ, ppm: 11.1, 14.4, 41.7, 49.5, 79.9, 77.5, 115.3, 150.4, 157.4. Mass spectrum (EI), *m/z* (I_{rel}, %): 194 (74, M^+), 165 (4), 122 (42), 94 (100), 78 (25), 51 (10). Found, %: C 55.2; H 7.0; N 28.56. $C_9H_{14}N_4O$. Calculated, %: C 55.65; H 7.27; N 28.85.

2-(3,3-Diethyltriaz-1-en-1-yl)pyridine-1-oxide (6f) . Yield 0.237 g (61%), oil. IR spectrum, ν, cm^{-1} : 3109–2870 br (CH), 1466 ($\delta_s CH_2$), 1377 ($\delta_s CH_3$). NMR ^1H spectrum (400 MHz, $CDCl_3$), δ, ppm: 1.25 t (3H, CH_3, *J* 7.2 Hz), 1.34 t (3H, CH_3, *J* 7.2 Hz), 3.82–3.87

q (2H, CH_2, *J* 7.2 Hz), 3.92–3.97 q (2H, CH_2, *J* 7.2 Hz), 7.00 t (1H, CH_{arom}, *J* 6.5 Hz), 7.29 t (1H, CH_{arom}, *J* 6.5 Hz), 7.44 d (2H, CH_{arom}, *J* 6.5 Hz), 8.24 d (1H, CH_{arom}, *J* 6.5 Hz). NMR ^{13}C spectrum (100 MHz, $CDCl_3$), δ, ppm: 10.9, 14.2, 43.0, 50.1, 115.0, 120.6, 129.0, 140.0, 156.3. Mass spectrum (EI), *m/z* (I_{rel}, %): 194 (50, M^+), 177 (8), 122 (12), 95 (10), 78 (100), 51 (7). Found, %: C 55.22; H 7.08; N 28.6. $C_9H_{14}N_4O$. Calculated, %: C 55.65; H 7.27; N 28.85.

CONCLUSION

It has been shown for the first time that 2-, 3-, and 4-aminopyridine-1-oxides **4** – **9** easily undergo diazotization in the presence of sulfonic acids. In this case, the 4-amino derivative **4**, unlike the 3-isomer **5**, gives stable diazonium salts, while the 2-amino derivative **6** forms oxotriazolpyridinium-2 sulfonates **6a–c** as stable isoelectronic forms of 2-diazonium-1-oxypyridine. In no case was the formation of covalent 1-oxypyridylsulfonates O-NPyOSO$_2$R observed, which is characteristic for the diazotization of aminopyridines. The obtained diazotization products readily interact with a number of nucleophiles, opening up new possibilities for the use of 2- and 4-aminopyridine-1-oxides in organic synthesis. The relative stability of diazonium cations in the pyridine, pyridine-1-oxide, and benzenediazonium cation series was determined by B3LYP/aug-cc-pVDZ quantum chemical calculations. The increased stability of 4-diazonium-1-oxypyridine **1c** in this series is confirmed by preparative results and ESI/MS and MS2 mass spectrometry data.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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