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Azulene-1-azopyridine 1′-oxides

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Abstract

The coupling between diazonium salts obtained from the three aminopyridine 1-oxides and azulene allowed the synthesis in good yield of the corresponding azulene-1-azopyridine 1′-oxides, which were characterised. The reduction and the methylation of the products were studied. The last two reactions allowed to synthesize azulene-1-azo-2′-pyridine and its alkylpyridinium salts, unavailable on other way. The UV–vis spectra of azulene-1-azopyridines were compared with those of the corresponding *N*-oxides and pyridinium salts. For the *N*-oxides the solvatochromic effect was evidenced.
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Keywords: Azulene; Diazene; Pyridine 1-oxides; Dyes

1. Introduction

Azulene-1-azo derivatives have been proven to be useful for their nonlinear optical properties (NLO) [1] and azopyridinium derivatives are well known for their photochromic, electrochemical and photoelectrochemical properties [2]. Therefore, we have decided to bring together the two mentioned functions in azulene-1-azopyridine derivatives and to study their synthesis and properties. In a previous paper [3] we have synthesized the isomers of azulene-1-azopyridines obtained from 3- and 4-aminopyridines. The impossibility to obtain the diazonium salt from the 2-isomer, the difficulties encountered in our attempts to obtain the diazonium salt of 4-aminopyridine [3] and to couple it with azulene suggested we should to find another way to synthesize the corresponding azo derivatives. Since the generation of the diazonium salts from pyridine 1-oxides is well known and occurs in high yields [4,5], we have investigated this possibility to reach after the azulene-1-azo-2′- and 4′-pyridine and their derivatives.

The diazonium salts obtained from 4- and especially from 2-aminopyridines are unstable in acidic medium due to the presence of a second positive charge at the pyridine moiety at an unfavourable position that promotes the *ipso*-nucleophilic substitution with N_2 elimination [6]. Therefore, either their use in the coupling reaction must be avoided or adequate reaction conditions must be chosen (for example, neutral or basic coupling medium) [1]. One of the solutions for lowering the positive

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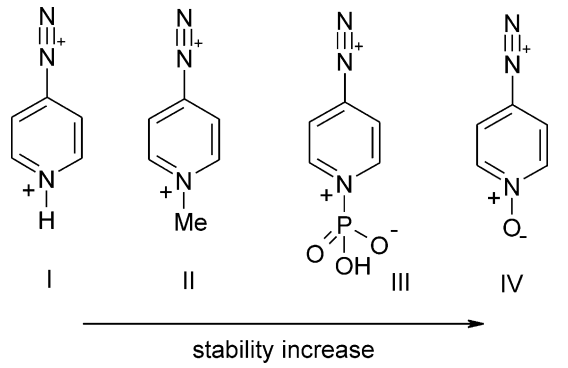


Scheme 1.

charge in pyridinium moiety consists in the complexation of the nitrogen atom as in pyridine 1-oxide.

From Scheme 1, which presents the estimated increase in stability for a few complexed diazonium salts obtained from 4-aminopyridine, it results that the coupling reaction with the 1-oxide seems to be the most favourable due to its possibility of forming a quinoide structure [7]. The diazotization of 4-aminopyridine 1-oxide worked six times faster than that for the 4-aminopyridine [4]. In spite of this fact, the best solution for the preparation of azulene-1-azo-4′-pyridine was the diazotization of the amine and the coupling in situ, in the presence of a polybasic acid in buffered medium (Scheme 1, structure III) [3] because it occurred in only one step in good yield.

Table 1
The diazotization of aminopyridine 1-oxides and the coupling of the salts with azulene

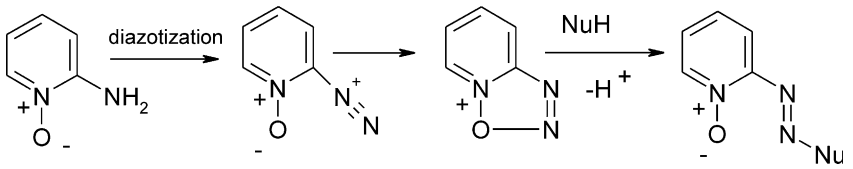
Azo compound	Azulene conversion (%)	Yield (%) (reported to the reacted azulene)
1	100	100
2	93.0	100
3	74.2	85.7

For the diazonium salt provided from 2-aminopyridine 1-oxide the closing of an unstable oxatriazole ring that can be easily attacked by the nucleophile (Scheme 2) [8] assists the stabilization.

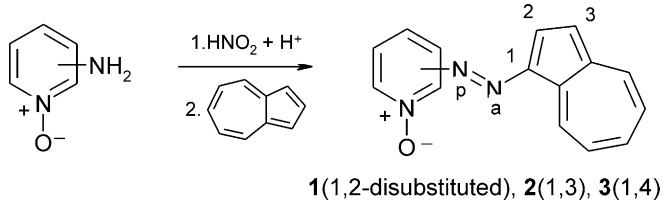
2. Results and discussion

2.1. Synthesis of N-substituted azulene-1-azopyridines and of azulene-1-azo-2′-pyridine

The reported experimental data about the coupling of diazonium salts obtained from aminopyridine1-oxides with easily oxidising nucleophiles or with hydrocarbons are relatively scarce. Therefore we have investigated the behaviour of azulene in presence of the diazotized aminopyridine 1-oxides (Scheme 3). The diazotization was performed in acidic aqueous media followed by the coupling with azulene in neutral medium and occurred in very good yields (Table 1). The azo compounds



Scheme 2.



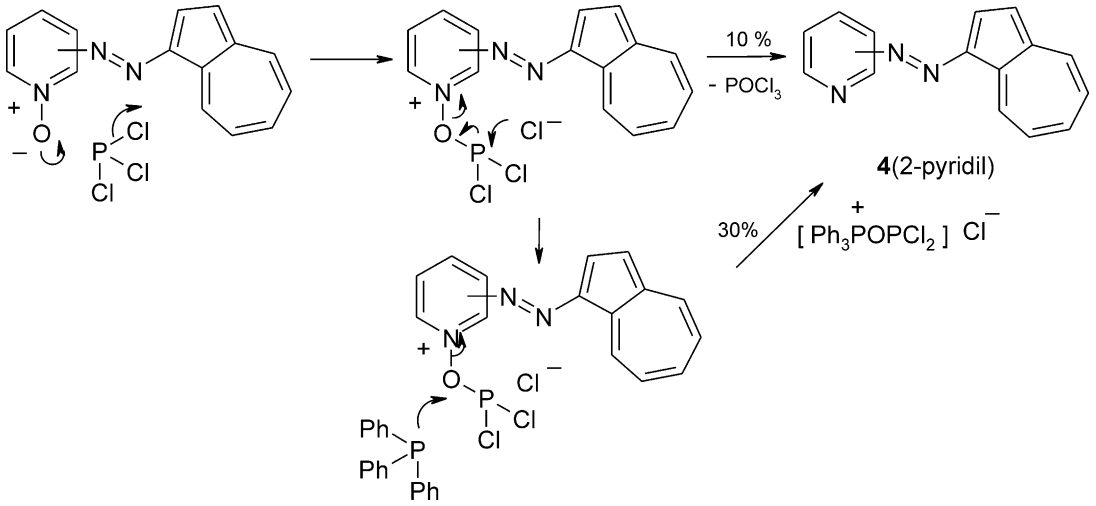
Scheme 3.

are sensitive to heating because they contain a reducing moiety, the azulene ring and an oxidant, the N–O group. For this reason they must be worked-up and manipulated at room temperature.

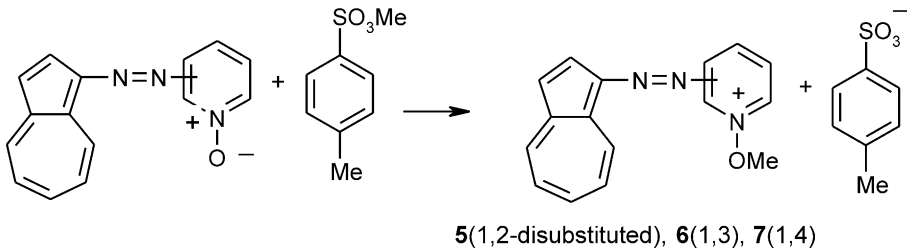
However, both the azulene moiety and the N=N bond are also sensitive to reducing agents therefore the elimination of the oxygen atom from the pyridine nitrogen for the generation of azulene-1-azopyridines represented a problem (especially for strong reducing agents). We have attempted to solve this problem by using metals in neutral media or P^{III} compounds as reductants. The reduction with metal failed because the reaction mixture had to be heated over 25 °C, therefore the destruction of the starting material took place. No reduction was observed when the azo derivatives were treated with triphenyl phosphine, possibly due to the nucleophilic character of the pyridine 1-oxide moiety. The use of PCl_3 alone was also unsatisfactory, generating tar to a high extent. Astonishingly, a mixture of $P(C_6H_5)_3$ and PCl_3 was most effective in the reduction. However, the conversion of starting materials and the reduction yields were low, therefore the procedure was used only for the synthesis of azulene-1-azo-2′-pyridine (**4**), inaccessible in other ways. A possible explanation for this behaviour is represented in Scheme 4 and it is based on the Lewis acid character of the phosphor halide and on the better reducing properties of the phosphine.

The interest for azulene-1-azo-1′-alkylpyridinium salts [3] suggested we should obtain these compounds by direct alkylation of the readily generated *N*-oxides. The reagents used by us for alkylation were the tosylates and iodides.

In dimethylformamide at 60 °C, methyl tosylate in equimolar ratio or in excess towards *N*-oxides produced the *O*-methylated product (**5**–**7**) (Scheme 5). Even in the presence of a high excess of tosylate, **1** and **3** were methylated in about 20% yield.



Scheme 4.



Scheme 5.

Table 2
Net charges for azulene-1-azopyridine 1′-oxides[a]

Position	1	2	3
N–O	−0.409	−0.431	−0.423
N–O	0.267	0.257	0.281
N_p=N	−0.097	−0.113	−0.147
N=N_a	−0.019	−0.058	−0.087
C–3	−0.120	−0.120	−0.138

[a] We have evaluated the oxidation potential by MO-calculations using a MOPAC package and MNDO approaches.

For the isomer 3′, (**2**), the tendency towards methylation in DMF was so low that the alkylation yield did not reach more than 7%. The loss of the alkyl group from the molecule, mainly for compound **7**, took place also in the presence of some nucleophilic agents (for example water). However, in the solvent-free reaction with an excess of reagent, 2′- and 4′-isomers (**1** and **3**), were *O*-alkylated in better yield (about 40%); the alkylation yield for **2** in the same conditions was 30%. The attempts to obtain a purified tosylates for the elemental analyses failed. Likewise, the very low volatility of the product hindered the recording of mass spectra. The characterisation of the tosylates was based on their clear and fairly clean NMR spectra.

The high tendency for *O*-alkylation can be understood when one examines the net charges in the molecules of compounds **1**–**3** (Table 2). The calculated values for the sites which could be nucleophilic attacked evidenced that the highest net charge is placed at the oxygen atom (the nitrogen atom bonded with oxygen shows an electrophilic character).

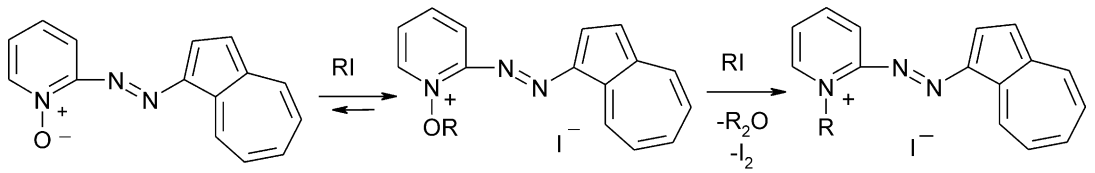
In the presence of an excess of alkyl iodide as methyl or *n*-buthl, *N*-alkylation took place in good conversions and yields (Scheme 6) against the predictions resulting from the calculated net charges for this position. Therefore, the electrophilic attack at this position cannot be involved. More experimental support must be found for the proposal of a possible *N*-alkylation mechanism.

This alkylation protocol represents a better way (only one step from *N*-oxide) to obtain azulene-1-azo-2′-(1′-alkylpiridinium) iodide (**8**), in comparison with the alkylation of **1** (two steps in low yield). For the easily obtainable azulene-1-azo-3′- and 4′-pyridine, the direct pyridine alkylation represents the best way.

2.2. Absorbtion spectra of azulene-1-azopyridines and their N-substituted derivatives

The results reported in Table 3 and in Scheme 7 show that the change from all azulen-1-azopyridines to their pyridiniums salts, methoxy or methyl, induces a strong bathochromic shift in the visible range and a rather small intense one in the near UV. That fact seems to indicate a good positive charge stabilization at pyridine nitrogen for the salts and similar electron distribution for all chromophore structures.

Appreciable differences in the bathochromic shifts can be observed, however, between the three isomers of azulene-1-azopyridine 1′-oxides. The intensity of bathochromic shift in the visible range increases in order **2** < **3** < **1**. The examination of the dipole structure of *N*-oxides **1** and **3** (Scheme 8) affords the existence of two important resonance structures (**A** and **B**) for the 2′- and 4′-isomers. The structures **1B** and **3B** are favoured by the tropylium stability. The long conjugated polyenic system present in these structures produces a bathochromic effect. The 3′-isomer (**2**), cannot

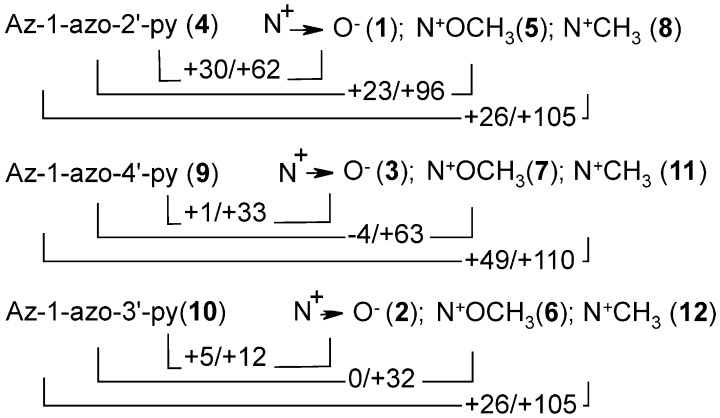


8 (R =Me), **13** (R =n-Bu)

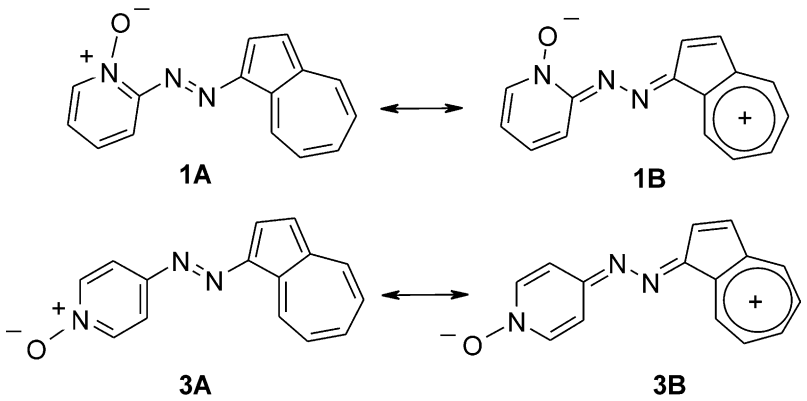
Scheme 6.

Table 3
UV–vis- spectra of azulene-1-azopyridines and their *N*-derivatives in methanol, λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1})

Compound	Band I	Band II	Band III	Band IV
Azulene-1-azo-2′-pyridine (**4**)	226 (4.36), 235 (4.30)	266sh (4.13), 273 (4.13)	319 (3.96)	410 (4.35)
N→O (**1**)	230 (4.34), 244 (4.56)	288 (4.12)	349 (3.87)	472 (4.41)
N→$^+$OCH$_3$ (**5**)	249 (4.15)	287 (4.11)	342 (3.83)	506 (4.20)
N→$^+$CH$_3$ (**8**)	227 (4.58), 247 (4.30)	288(4.02), 306 (3.94)	345 (3.83)	515 (4.46)
Azulene-1-azo-4′-pyridine (**9**)	215 (4.32), 234 (4.29)	285 (4.13)	339 (3.92)	439 (4.39)
N→O (**3**)	230 (4.35)	286 (4.23), 294 (4.21)	340 (3.95)	472 (4.50)
N→$^+$OCH$_3$ (**7**)	232 (4.15)	273 (4.18)	335 (3.82)	502 (4.17)
N→$^+$CH$_3$ (**11**)	230 (4.60), 253 (4.28)	280 (4.12)	389 (3.84)	539 (4,26)
Azulene-1-azo-3′-pyridine (**10**)	235 (4.31)	280 (4.20)	337 (3.94)	434 (4.38)
N→O (**2**)	241 (4.30)	294 (4.23)	342 (3.94)	446 (4.42)
N→$^+$OCH$_3$ (**6**)	219 (4.48), 246 (4.29)	284 (4.00)	337 (3.82)	466 (4.03)
N→$^+$CH$_3$ (**12**)	210(4.46), 223 (4.55), 258 (4.21)	305 (4.00)	363 (3.87)	539 (4.39)



Scheme 7. Difference between the band III/bands IV (in nm).



Scheme 8.

Table 4
The solvent effect on the visible absorption band of azulene-1-azopyridine 1′-oxides, λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1})

	Solvent						
	C_6H_{12}	Toluene	Acetone	CH_3CN	DMF	CH_3OH	Water
1	448 (4.28)	449 (4.29)	446 (4.28)	450 (4.25)	472 (4.34)	472 (4.41)	481 (4.41)
2	428 (4.37)	436 (4.34)	434 (4.38)	436 (4.38)	443 (4.38)	445 (4.42)	461 (4.42)
3	461 (4.45)	466 (4.47)	460 (4.46)	460 (4.46)	472 (4.46)	472 (4.50)	484 (4.49)

Table 5
Elemental analyses: calcd (found)%

Compd	Mp °C	Formula	C	H	N	Halogen
1	190 (DCM).	$C_{15}H_{11}N_3O$	72.28 (72.07)	4.45 (4.59)	16.86 (16.76)	–
2	130 (DCM).	$C_{15}H_{11}N_3O$:	72.28 (72.27)	4.45 (4.49)	16.86 (16.66)	–
3	202 (DCM)	$C_{15}H_{11}N_3O$	72.28 (72.14)	4.45 (4.50)	16.86 (16.78)	–
4	190 (DCM)	$C_{15}H_{11}N_3$	77.23 (77.27)	4.75 (4.69)	18.02 (18.04)	–
8	171 ($CHCl_3$)	$C_{16}H_{14}IN_3$	51.22 (51.30)	3.76 (3.80)	11.20 (11.04)	33.82 (33.86)
13	272 ($CHCl_3$)	$C_{19}H_{20}IN_3$	54.69 (54.82)	4.83 (4.87)	10.07 (10.05)	30.41 (30.26)

Table 6
IR spectra

Compd	ν (KBr) cm^{-1}
1	1460 (m), 1605 (m), 2310 (m), 2330 (m), 2370 (m), 2410 (m), 2525 (m), 2690 (m), 3010 (m), 3080 (m), 3690 (m).
2	610 (m), 665 (m), 740 (m), 780 (m), 870 (m), 965 (m), 1015 (m), 1130 (m), 1275 (m), 1360 (m), 1445 (m), 2360 (m).
3	460 (m), 485 (m), 525 (m), 567 (m), 745 (m), 767 (m), 850 (m), 915 (m), 922 (m), 945 (m), 1096 (m), 1145 (m), 1208 (m), 1267 (m), 1320 (m), 1356 (m), 1390 (m), 1412 (m), 1435 (m), 1449 (m), 1475 (m), 1570 (m), 1600 (m), 3030 (m).
5	570 (m), 675 (m), 760 (m), 820 (m), 1010 (s), 1040 (m), 1230 (s), 1270 (m), 1305 (s), 1340 (m), 1400 (s), 1495 (m), 1560 (m), 1590 (s), 2370 (m), 3075 (m).
7	530 (m), 570 (m), 680 (m), 740 (m), 775 (m), 840 (m), 1010 (s), 1040 (m), 1140 (m), 1200 (s), 1270 (m), 1310 (s), 1340 (m), 1390 (m), 1450 (m), 1475 (m), 1530 (m), 1570 (m), 1600 (m), 1615 (m), 2240 (m), 2280 (m), 3020 (m).
8	685 (m), 730 (m), 745 (m), 775 (m), 815 (m), 895 (m), 1020 (s), 1130 (m), 1150 (m), 1220 (s), 1230 (m), 1240 (m), 1290 (s), 1320 (m), 1435 (m), 1470 (m), 1565 (m), 1610 (s), 2380 (m), 2920 (m), 3020 (m), 3050 (m).
13	635 cm^{-1} (m), 730 (m), 745 (m), 775 (m), 805 (m), 890 (m), 1020 (s), 1110 (m), 1130 (m), 1205 (s), 1230 (m), 1260 (m), 1280 (s), 1320 (m), 1440 (m), 1450 (m), 1560 (m), 1610 (s), 1720 (m), 2380 (m), 2850 (m), 2920 (m), 2950 (m).

adopt such a structure and, as a result, the effect on the colour of *N*-oxide is lower. This assertion can be proved by the solvatochromic effect characteristic for dipolar structures. The data from the Table 4 reveal an important bathochromic shift that increases with polarity of the solvent for compounds **1** and **3** and almost the same values for the compound **2**. That means that the contribution of structures with great separation between the charges increase with the polarity of the solvent. The most pronounced solvatochromic effect for the compound **1** can be explained by the difference in the length of two conjugated systems in structure is **1B** and **3B**.

3. Conclusions

The coupling between diazonium salts obtained from amino pyridine 1-oxides and azulene allowed us to obtain and characterize the three possible azulene-1-azopyridine 1′-oxides and to study their reduction and methylation. We have found that alkylation with methyl tosylate occurred at the oxygen atom and with an excess of methyl iodide at the nitrogen of the N–O bond. The reduction of isomer **1** represents the only convenient way for the synthesis of azulene-1-azo-2′-pyridine. The *N*-alkylpyridinium salts of the last azo derivative were directly and in good yield generated by the alkylation of **1** at the nitrogen of pyridine 1-oxide moiety. Therefore, this protocol is preferred to the alkylation of the pyridine moiety. Studies about the nonlinear optical properties of some of the reported compounds are in progress.

The change from the azulene-1-azopyridines to the corresponding pyridinium derivatives, N^+OCH_3 and N^+CH_3 produces a bathochromic effect for all isomers. The strong bathochromic effect observed only at compounds **1** and **3** by pyridine nitrogen substitution with oxygen in *N*-oxides was explained by the electron distribution in the dipolar structures. This explanation was supported by the existence of the solvatochromic effect for the two isomers, as well.

4. Experimental

Melting points: Kofler apparatus (Reichert Austria). Elemental analyses: Perkin Elmer CHN 240B. UV spectra: Beckman DK-2A, UV 5240. ^{1}H- and ^{13}C NMR spectra in $CDCl_3$ or DMSO-d_6: Bruker WM 300, AC 300, ARX 300 and Gemini 300 (^{1}H: 300 MHz, ^{13}C: 75.47 MHz), TMS was used as internal standard (for $CDCl_3$); when necessary, unequivocal signal assignment was confirmed by the analysis of the corresponding ^{1}H–^{1}H COSY and ^{1}H–^{13}C HETCOR spectra. Mass spectra: Finnigan MAT 311-A/100 MS. Column chromatography: basic alumina (activity BII-III (Brockmann)). All eluted solutions were filtered before concentration. The dichloromethane (DCM) was distilled over calcium hydride and ethyl acetate over anhydrous sodium carbonate, chloroform was filtered on basic alumina. The dimethylformamide (DMF) was distilled. The aminopyridine-*N*-oxides were prepared using known protocols (2-aminopyridine 1-oxide [9], 3-aminopyrine 1-oxide [10] and 4-aminopyridine 1-oxide [11]).

4.1. Synthesis of Azulene-1-azopyridine 1′-oxides

4.1.1. Azulene-1-azo-2′-pyridine 1′-oxide (*1*)

2-Aminopyridine 1-oxide chlorohydrate (842 mg, 5.75 mmol) was dissolved in 5 M HCl (5.2 ml) and the solution was cooled to −5 °C. Sodium nitrite (518 mg, 7.5 mmol) was dissolved in water (5 ml) and after cooling at 0 °C it was added to the first solution. The generated clear, yellow diazonium salt was stirred for 5 min at 0 °C and was poured under stirring into a solution of azulene (640 mg, 5 mmol) and potassium acetate (3.4 g) dissolved in methanol (25 ml). The solution turned red almost instantaneously. It was left for 30 min at 0 °C and then neutralised with concentrated sodium carbonate solution. The solution was diluted with water (75 ml) and extracted with DCM (4×100 ml). The organic solution was washed with water (200 ml) and then dried (Na_2SO_4 anh.). The solvent was partially evaporated under vacuum at room temperature and the residual solution was chromatographed on silicagel using DCM for elution of azulene and methanol for elution of the azo derivative. The first fraction (blue) represented azulene (a very small amount); the residue from the second fraction (brown), after the solvent vaporisation in vacuum at room temperature, was characterized as product **1** (1.25 g, yield 100% reported to azulene).

4.1.2. Azulene-1-azo-3′-pyridine 1′-oxide (*2*)

The same procedure as described above was used for the diazotization and coupling of 3-aminopyridine 1-oxide. The ratio between the reagents for the generation of the diazonium salt was 1:1 and the diazonium salt was used in 50% excess reported to azulene. The recovered azulene represented 7% and the yield in **2** was 100%.

*4.1.3. Azulene-1-azo-4′-pyridine 1′-oxide (**3**)*

4-Aminopyridine 1-oxide was coupled in the same conditions using a molar ratio amine:sodium nitrite:azulene = 1:2:1. The coupling was performed for 30 min at 0 °C and 2 h at room temperature. The first fraction resulted by the chromatographic separation (blue) represented azulene, (conversion 74.2%), the second fraction in very low quantity (brown) was unidentified and the third fraction (brown) represented the product **3** in 85.7% yield.

4.1.4. Reduction with P^{III} compounds

Azulene-1-azo-2′-pyridine 1′-oxide (**1**) (125 mg, 0.5 mmol) was dissolved in DCM (3 ml) and PPh_3 (130 mg, 0.5 mmol) and PCl_3 (83 mg, 0.6 mmol) were added at 0 °C with stirring. The reaction mixture turned green and the stirring at 0 °C was continued for 1 h (if the reaction mixture reached room temperature the yield was very low). Then a solution of NaOH (4 ml, 5%) was added under good cooling. The solution was extracted four times with DCM, the organic layer was dried (Na_2SO_4 anh.) and the solvent was evaporated at room temperature. The residue was chromatographed twice on alumina columns. The first chromatographic separation eluent DCM–EtOH 9:1 was performed for the retention of the tar product. From the second chromatography with benzene-ethyl acetate (from 0 to 50% ester), two fractions were separated: a first significant fraction (brown), azulene-1-azo-2′-pyridine (**4**) (17 mg, 35.1%)— and a second fraction (red-brown) the starting material (**1**) (73 mg, conversion 41.6%).

4.2. O-alkylation of azopyridine 1′-oxides

*4.2.1. Azulene-1-azo-3′-(1′-methoxypyridinium) tosylate (**6**)*

(A) A preparation using a solvent. Azulene-1-azo-3′-pyridine 1′-oxide (**2**) (25 mg, 0,1 mmol) and methyl tosylate (190 mg, 1 mmol) were dissolved in DMF (1 ml) and the reaction mixture was heated at 60 °C with 5 h stirring. The reaction mixture was let to reach the room temperature and it was chromatographed on alumina with DCM as eluent. The first coloured fraction (brown) was azo compound **2**. The second fraction (red) was eluted with DCM–EtOH = 1:1 and represents the desired *O*-methylated product (3 mg 7%, without the starting material recovery). The *O*-alkylated products are hydrolysed on Al_2O_3 or SiO_2 therefore their purification by column chromatography is not recommended.

(B) A preparation without a solvent. A mixture of compound **2** (0.1 mmol) and methyl tosylate (1 mmol) was conserved 3 days at room temperature. The obtained mixture was treated with diethyl ether for the recovery of starting reagents that were soluble and the resulted methylated product was filtered and washed on the filter with a small amount of ether. The obtained yield in *O*-methylated product (**6**), was 32.2%.

*4.2.2. Azulene-1-azo-2′-(1′-methoxypyridinium) tosylate (**5**)*

By procedure B, after 4 h at room temperature, the yield in *O*-methylated product was 44%.

*4.2.3. Azulene-1-azo-4′-(1′-methoxypyridinium) tosylate (**7**)*

By procedure A, the yield of *O*-methylated product was 25%. By procedure B, after several hours at room temperature the yield in *O*-methylated product was 41%. When the reaction start was difficult, several drops of DMF were added. The heating of the reaction mixture until 40 °C was sometimes recommended, however, in this case carefully TLC monitoring was necessary. The tosylate (**7**) was unstable at conservation: it was fast dealkylated after the separation from the excess of methyl tosylate and then it was transformed into a tar. For this reason it was not completely characterised (see the Experimental section).

4.3. N-alkylation of azulene-1-azo-2′-pyridine 1′-oxide with oxygen elimination

4.3.1. N-methylation

Azulene-1-azo-2′-pyridine 1′-oxide (50 mg, 0.2 mmol) and CH_3I (1 ml, large excess) were dissolved in chloroform (5 ml) and the solution was refluxed with stirring for 1 h. Then, CH_3I (1 ml) was supplementary added and the reflux was continued for 1 h. The reaction mixture was poured into an alumina column and eluted with DCM–MeOH

(0–10% methanol). The first fraction (brown) represents the starting material (10 mg, conversion 80%) and the second band (dark red) was the *N*-alkylated product, azulene-1-azo-2′-(1′-methylpyridinium) iodide (**8**) (41 mg, 68.4%).

4.3.2. N-butylation

Azulene-1-azo-2′-pyridine 1′-oxide (30 mg, 0.12 mmol) and *n*-butyl iodide (1 ml) were dissolved in chloroform (3 ml). The reaction mixture was stirred for 4 h at reflux, let to stay overnight at room temperature and then chromatographed on silica gel, using a mixture of DCM–MeOH (20:1) as eluent. The first fraction (brown) represented the starting material (19 mg, conversion 36.7%) and the second fraction (violet) contained azulene-1-azo-2′-(1′-butylpyridinium) iodide (**13**), (11 mg, 0.026 mmol, 59.9%).

*4.3.3. Other procedures for the synthesis of azulene-1-azo-2′-(1′-alkyl-pyridinium) iodide (**8**)*

(a) A procedure by directly azo coupling. By the classical coupling of the azulene with diazonium salt obtained from the 2-amino-1-methylpyridinium iodide, the pyridinium salt **8** was generated in very small yield (<5%).

(b) Azulene-1-azo-2′-pyridine methylation. The azo derivative (100 mg, 0.429 mmol) and methyl iodide (5 ml) were dissolved in chloroform (30 ml). The reaction mixture was stirred for 1 h at reflux and then methyl iodide (5 ml) was supplementary added and the heating was continued for 1 h. The reaction mixture was separated on alumina, eluent: DCM–MeOH = 20:1. The major violet fraction represented alkylated azo derivative **8** (153 mg, 95.1%).

4.4. Product characterisation

The elemental analyses are presented in Table 5 and IR spectra in Table 6.

*4.4.1. Azulene-1-azo-2′-pyridine 1′-oxide (**1**)*

Dark brown crystals. ^{1}H NMR ($CDCl_3$) δ 7.20 (ddd, J = 7.4, 6.5, 2.1 Hz, 1H, 5′-H), 7.32 (ddd, J = 8.2, 7.4, 1.4 Hz, 1H, 4′-H), 7.46 (d, J = 4.7 Hz, 1H, 3-H), 7.49 (tt, J = 9.7, 0.7 Hz, 1H, 5-H), 7.60 (tt, J = 9.8, 0.8 Hz, 1H, 7-H), 7.85 (tt, J = 9.4, 0.6 Hz, 1H, 6-H), 7.91 (dd, J = 8.4, 2.0 Hz, 1H, 3′-H), 8.37 (dd, J = 6.4, 1.4 Hz, 6′-H), 8.38 (d, J = 9.6 Hz, 1H, 4-H), 8.55 (d, J = 4.7 Hz, 1H, 2-H), 9.33 (d, J = 9.7 Hz, 1H, 8-H). ^{13}C NMR ($CDCl_3$) δ 114.5 (C-3′), 122.0 (C-3), 124.2 (C-5′), 125.7 (C-2), 127.8 (C-5), 128.9 (C-7), 129.0 (C-4′), 135.9 (C-8), 139.0 (C-4), 140.1 (C-6), 140.8 (C-6′), 141.2 (C-8a), 145.7 (C-3a), 146.3 (C-1), 158.9 (C-2′). m/z: 249 (M^+, 3%), 233 (M–[O], 1), 219 (M^+–[N_2–$^+$H], 1), 205 (M–[N_2–O], 17), 204 (61), 176 (3), 155 ([AzN_2], 2), 143 (25), 140 (11), 127 ([Az], 100), 115 ([C_9H_7], 13), 101 (13), 77 ([C_6H_5], 28).

*4.4.2. Azulene-1-azo-3′-pyridine 1′-oxide (**2**)*

Brown crystals. ^{1}H NMR ($CDCl_3$) δ 7.38 (dd, J = 7.9, 6.4 Hz, 1H, 5′-H), 7.46 (d, J = 4.7 Hz, 1H, 3-H), 7.46 (t, J = 9.7 Hz, 1H, 5-H), 7.58 (t, J = 9.9 Hz, 1H, 7-H), 7.85 (t, J = 9.9 Hz, 1H, 6-H), 7.86 (ddd, J = 8.3, 1.7, 0.9 Hz, 1H, 4′-H), 8.19 (dt, J = 6.4, 0.7 Hz, 1H, 6′-H), 8.27 (d, J = 4.5 Hz, 1H, 2-H), 8.39 (d, J = 9.3 Hz, 1H, 4-H), 8.83 (t, J = 1.6 Hz, 1H, 2′-H), 9.29 (d, J = 9.9 Hz, 1H, 8-H). ^{13}C NMR ($CDCl_3$) δ 120.6 (C-5′), 121.4 (C-3), 125.3 (C-4′), 125.5 (C-2), 128.4 (C-7), 128.5 (C-5), 133.0 (C-2′), 135.6 (C-8), 138.0 (C-6′), 139.1 (C-4), 140.2 (C-6), 140.9 (C-8a), 143.9 (C-3a), 145.3 (C-1), 152.2 (C-3′). m/z: 250 (M^+ + 1, 2), 249 (M^+, 13), 233 (M^+–[O], 2), 220 (M^+–[N_2–H], 2), 204 (7), 192 (7), 165 (5), 155 ([AzN_2], 4), 140 (6), 127 ([Az], 100), 101 (9), 77 ([C_6H_5], 20).

*4.4.3. Azulene-1-azo-4′-pyridine 1′-oxide (**3**)*

Black crystals. ^{1}H NMR ($CDCl_3$) δ 7.42 (t, J = 9.7 Hz, 1H, 5-H), 7.43 (d, J = 4.2 Hz, 1H, 3-H), 7.52 (t, J = 9.7 Hz, 1H, 7-H), 7.80 (d, J = 7.4 Hz, 2 H, 3′-H, 5′-H), 7.81 (t, J = 9.6 Hz, 1H, 6-H), 8.24 (d, 2H, J = 7.4 Hz, 2′-H, 6′-H), 8.25 (d, J = 4.5 Hz, 1H, 2-H), 8.34 (d, J = 9.8 Hz, 1H, 4-H), 9.22 (d, J = 9.8 Hz, 1H, 8-H). ^{13}C NMR ($CDCl_3$) δ 118.5 (C-3′, C-5′), 121.5 (C-3), 125.3 (C-2), 128.1 (C-7), 128.2 (C-5), 135.5 (C-8), 139.8 (C-2′, C-6′), 139.0 (C-4), 140.2 (C-6), 140.4 (C-8a), 144.4 (C-3a), 145.3 (C-1), 150.3 (C-4′). m/z: 249 (M^+, 10), 233 (M^+–[O], 10), 155 ([AzN_2], 9), 127 ([Az], 100).

*4.4.4. Azulene-1-azo-2′-pyridine (**4**)*

Brown crystals. ^{1}H NMR ($CDCl_3$) δ 7.30 (ddd, J = 7.2, 4.9, 1.2 Hz, 1H, 5′-H), 7.41 (t, J = 9.8 Hz,

1H, 5-H), 7.45 (d, $J=4.4$ Hz, 1H, 3-H), 7.52 (t, $J=9.8$ Hz, 1H, 7-H), 7.80 (t, $J=9{,}8$ Hz, 1H, 6-H), 7.86 (ddd, $J=8.2$, 7.3, 1.8 Hz, 1H, 4′-H), 7.94 (t, $J=8.2$, 1.2 Hz, 1H, 3′-H), 8.37 (d, $J=9.2$ Hz, 1H, 4-H), 8.46 (d, $J=4.7$ Hz, 1H, 2-H), 8.72 (dd, $J=5.0$, 1.8 Hz, 1H, 6′-H), 9.39 (1H, d, $J=9.9$ Hz, 8-H). ^{13}C NMR ($CDCl_3$) δ 113.0 (C-3′), 120.7 (C-3), 123.4 (C-5′), 126.2 (C-2), 127.6 (C-5, C-7), 135.7 (C-8), 137.8 (C-4′), 138.7 (C-4), 139.8 (C-6), 140.0 (C-8a), 144.2 (C-3a), 144.9 (C-1), 149.3 (C-6′). 164.8 (C-2′).

*4.4.5. Azulene-1-azo-2′-(1′-methoxypyridinium) tosylate (**5**)*

Dark red crystals. ^{1}H NMR (DMSO-d_6) δ 2.29 (s, 3 H, C*H*$_3$-(C-4″)), 4.46 (s, 3 H, C*H*$_3$O), 7.10 (d, $J=7.6$ Hz, 2 H, 3″-H, 5″-H), 7.49 (d, $J=8.0$ Hz, 2 H, 2″-H, 6″-H), 7.78 (d, $J=4.8$ Hz, 1H, 3-H), 7.79 (dd, $J=7.6$, 6.4 Hz, 1H, 5′-H), 8.09 (t, $J=9.2$ Hz, 1H, 5-H), 8.18 (t, $J=9.2$ Hz, 1H, 7-H), 8.23 (d, $J=4.8$ Hz, 1H 2-H), 8.36 (t, $J=9.2$ Hz, 1H, 6-H), 8.42 (dd, $J=8.0$, 7.6 Hz, 1H, 4′-H), 8.52 (d, $J=8.4$ Hz, 1H, 3′-H), 8.83 (d, $J=9.2$ Hz, 1H, 4-H), 9.18 (d, $J=6.4$ Hz, 1H, 6′-H), 9.51 (d, $J=9.9$ Hz, 1H, 8-H). ^{13}C NMR (DMSO-d_6) δ 20.73 (*C*H$_3$–(C-4″)), 69.11 (*C*H$_3$O), 116.2 (C-3′), 123.5 (C-3), 125.5 (C-2, C-2″, C-6″), 127.9 (C-5′), 128.1 (C-3″, C-5″), 136.2 (C-5, C-7), 137.7 (C-1″, C-8), 140.5 (C-6′), 142.1 (C-4), 144.2 (C-6), 144.3 (C-4′), 144.8 (C-8a), 145.7 (C-4″), 146.9 (C-3a), 151.3 (C-1), 156.4 (C-2′).

*4.4.6. Azulene-1-azo-3′-(1′-methoxypyridinium) tosylate (**6**)*

Brown crystals. ^{1}H NMR (DMSO-d_6) δ 2.27 (s, 3H, C*H*$_3$–(C-4″)), 4.54 (s, 3H, C*H*$_3$O), 7.10 (d, $J=7.8$ Hz, 2H, 2″-H, 6″-H), 7.49 (d, $J=7.8$ Hz, 2H, 3″-H, 5″-H), 7.69 (d, $J=4.6$ Hz, 1H, 3-H), 7.79 (t, $J=9.7$ Hz, 1H, 5-H), 7.89 (t, $J=9.7$ Hz, 1H, 7-H), 8.16 (t, $J=9.9$ Hz, 1H, 6-H), 8.22 (d, $J=4.7$ Hz, 1H, 2-H), 8.30 (dd, $J=8.3$, 6.6 Hz, 1H, 5′-H), 8.73 (d, $J=9.4$ Hz, 1H, 4-H), 8.98 (d, $J=8.7$ Hz, 1H, 4′-H), 9.37 (d, $J=6.6$ Hz, 1H, 6′-H), 9.55 (d, $J=9.7$ Hz, 1H, 8-H), 9.98 (s, 1H, 2′-H). ^{13}C NMR (DMSO-d_6) δ 20.80 (*C*H$_3$–(C-4″)), 69.87 (*C*H$_3$O), 123.3 (C-3), 124.6 (C-2), 125.5 (C-2″, C-6″), 128.1 (C-3″, C-5″), 129.2 (C-5′), 131.1 (C-7), 131.2 (C-5), 134.1 (C-2′), 135.6 (C-4′), 137.5 (C-1″), 137.7 (C-8), 138.5 (C-6′), 140.9 (C-4), 142.2 (C-8a), 142.3 (C-6), 143.8 (C-3a), 145.7 (C-4″), 146.1 (C-1), 153.0 (C-3′).

*4.4.7. Azulene-1-azo-4′-(1′-methoxypyridinium) tosylate (**7**)*

^{1}H NMR ($CDCl_3$) δ 2.28 (s, 3H, C*H*$_3$–(C-4″)), 4.43 (s, 3H, C*H*$_3$O), 7.12 (d, $J=8.3$Hz, 2H, 3″-H, 5″-H), 7.49 (d, $J=8.1$Hz, 2H, 2″-H, 6″-H), 7.78 (d, $J=4.8$ Hz, 1H, 3-H), 8.00 (t, $J=9.7$ Hz, 1H, 5-H), 8.09 (t, $J=9.8$ Hz, 1H, 7-H), 8.27 (s, 1H, 2-H), 8.30 (t, $J=9.9$ Hz, 1H, 6-H), 8.39 (bd$_{AB}$, $J=7.2$Hz, 2H, 3′-H, 5′-H), 8.82 (d, $J=9.2$Hz, 1H, 4-H), 9.36 (bd$_{AB}$ $J=7.2$Hz, 2H, 2′-H, 6′-H), 9.59 (d, $J=9.9$ Hz, 1H, 8-H). ^{13}C NMR (DMSO-d_6) δ 20.80 (*C*H$_3$–(C-4″)), 118.9 (C-3′, C-5′), 122.0 (C-3), 125.5 (C-2″, C-6″), 125.7 (C-2), 128.1 (C-3″, C-5″), 129.2 (C-7), 129.3 (C-5), 135.8 (C-8), 137.5 (C-1″), 140.3 (C-2′, C-6′), 139.2 (C-4), 140.3 (C-6), 142.0 (C-8a), 144.8 (C-3a), 145.7 (C-4″), 149.2 (C-1), 162.0 (C-4′).

*4.4.8. Azulene-1-azo-2′-(1′-methylpyridinium) iodide (**8**)*

Dark red crystals. ^{1}H NMR (DMSO-d_6) δ 4.47 (s, 3H, C*H*$_3$), 7.80 (ddd, $J=7.6$, 6.3, 1.4 Hz, 1H, 5′-H), 7.83 (d, $J=4.4$ Hz, 1H, 3-H), 8.06 (t, $J=9.7$ Hz, 1H, 5-H), 8.15 (t, $J=9.8$ Hz, 1H, 7-H), 8.35 (t, $J=9.9$ Hz, 1H, 6-H), 8.37 (ddd, $J=8.3$, 7.6, 1.2Hz, 1H, 4′-H), 8.48 (d, $J=4.5$ Hz, 1H, 2-H), 8.48 (dd, $J=8.3$, 1.3Hz, 1H, 2-H), 8.86 (d, $J=9.9$ Hz, 1H, 4-H), 8.87 (d, $J=6.3$, 1.2Hz 1H, 6′-H), 9,57 (d, $J=9.9$ Hz, 1H, 8-H). ^{13}C NMR (DMSO-d_6) δ 43.1 (*C*H$_3$), 114.2 (C-3′), 123.4 (C-5′), 126.1 (C-3), 126.5 (C-2), 134.9 (C-5, C-7), 137.5 (C-8), 141.8 (C-4), 143.7 (C-6), 144.6 (C-4′), 144.8 (C-6′), 145.2 (C-8a), 146.9 (C-3a), 150.0 (C-1), 157.6 (C-2′).

*4.4.9. Azulene-1-azo-2′-(1′-butylpyridinium) iodide (**13**)*

Black crystals. ^{1}H NMR (DMSO-d_6), δ 1.03 (t, $J=7.4$ Hz, 1H, C*H*$_3$CH$_2$), 1.53 (sextet, $J=7.4$ Hz, 1H, CH$_3$C*H*$_2$), 2.05 (heptet, $J=7.4$ Hz, 1H, CH$_2$C*H*$_2$CH$_2$), 5.04 (t, $J=7.4$ Hz, 1H, C*H*$_2$N), 7.63 (d, $J=4.9$ Hz, 1H, 3-H), 7.74 (ddd, $J=7.9$, 6.4, 0.9 Hz, 1H, 5′-H), 7.96 (t, $J=9.9$ Hz, 1H, 5-H), 8.09 (t, $J=9.9$ Hz, 1H, 7-H), 8.24 (t, $J=9.9$ Hz, 1H, 6-H), 8.24 (d, $J=4.6$ Hz, 1H, 2-H). 8.39 (dt, $J=8.3$, 7.9, 0.6 Hz, 1H, 4′-H), 8.46 (dd,

$J = 8.3$, 0.8 Hz, 1H, 3′-H), 8.64 (d, $J = 9.5$ Hz, 1H, 4-H), 9.05 (d, $J = 6.4$, 0.6 Hz, 1H, 6′-H), 9.53 (d, $J = 9.3$Hz, 1H, 8-H). ^{13}C NMR (DMSO-d_6) δ 13.37 (CH_3), 18.79 (CH_3CH_2), 32.74 ($CH_3CH_2CH_2$), 55.47 (CH_2N), 114.7 (C-3′), 123.2 (C-5′), 125.9 (C-3), 126.7 (C-2), 134.6 (C-5), 134.5 (C-7), 137.2 (C-8), 140.8 (C-4), 142.7 (C-6), 143.3 (C-4′), 144.4 (C-6′), 145.2 (C-8a), 146.5 (C-3a), 150.0 (C-1), 157.6 (C-2′). UV–vis (methanol) λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 223 (4.52), 245 sh (4.27), 288 (4.06), 337 (3.85), 506 (4.39), 698 (2.80).

References

[1] Lacroix PG, Malfant I, Iftime G, Razus AC, Nakatani K, Delaire JA. Chem Eur J 2000;6(14):2599–608.

[2] Nakagawa M, Rikukawa M, Watanabe M, Sanui K, Ogata N. Bull Chem Soc Jpn 1997;70:737–44.

[3] Razus AC, Birzan L, Nae S, Razus SA, Cimpeanu V, Stanciu C. Synth Commun 2002;32:825–37.

[4] Putter R. In: Muller E, editor. Methoden der organischen chemie (Houben-Weil), vol 10/3. Stuttgart: Georg Thieme Verlag; 1965. p. 53–66.

[5] Das PJ, Khound S, Dutta J. Indian J Chem 1995;34 B:161–3.

[6] Kalatzis E, Mastrokalos C. J Chem Soc, Perkin Trans 1977;2:1830–5.

[7] Ochiai E. J Org Chem 1953;18:534–51.

[8] Becker HGO, Bottcher H, Haufe H. J Prakt Chem 1970; 312:433–9.

[9] Deady LW. Synth Commun 1977;7:509–14.

[10] Jones RA, Katrizky AR. J Chem Soc 1960: 2937–42. Leonard F, Wajngurt A. J Org Chem 1956: 21, 1077–81.

[11] Undheim K, El-Gendy MAF, Hurum T. Acta Chemica Scandivica B 1974;28:743–9.