Synthesis and properties of 4-(3-Substituted azulen-1-yl)-2,6-diphenylpyridines

Alexandru C. Razus, Liviu Birzan*, Andreea Corbu, Oana Zaharia, and Cristian Enache

Institute of Organic Chemistry "C. D. Nenitzescu" of Romanian Academy, Spl. Independentei 202B, PO Box 35-108, 060023-Bucharest, Romania
E-mail: lbirzan@cco.ro

Abstract
The syntheses of 4-azulen-1-yl-2,6-diphenylpyridines substituted at the azulene C-3 moiety with electron donating or withdrawing groups, are reported. When electron-donating groups (EDG) are present, the reaction of the corresponding pyranylium perchlorates and ammonium acetate takes place. Because of the difficulties in the generation of pyranylium salts with electron-withdrawing groups (EWG), the corresponding pyridines are obtained by a $PdCl_2$-promoted substitution of halogen in 4-chloro-2,6-diphenylpyranylium salt, with an azulene derivative followed by an *in situ* replacement of oxygen with nitrogen. The physical and chemical properties of the pyridines obtained are discussed.

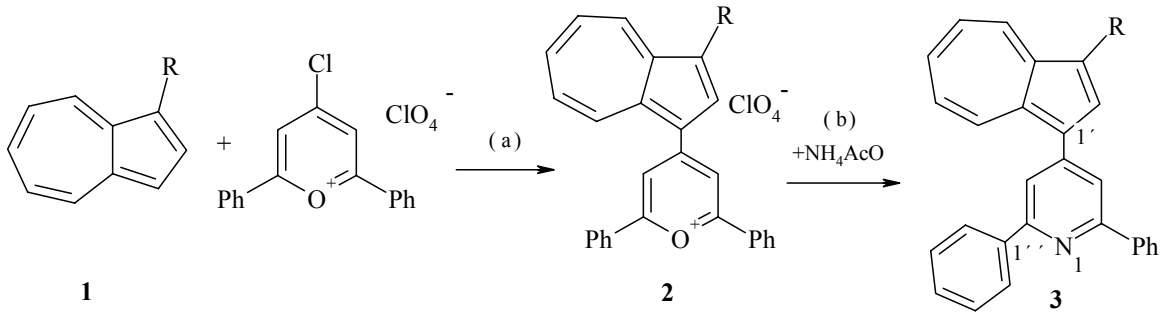
Keywords: Pyridine, palladium salt-promoted coupling, pyranylium salt, azulene

Introduction

As a part of our interest in the chemistry of azulenes, we have reported recently the synthesis of new 2,6-dimethyl and 2,6-diphenylpyranylium salts substituted at the 4-position with an azulen-1-yl group by the reaction of the corresponding azulenes with 4-chloro-2,6-disubstituted pyranylium salts. Good results are obtained when azulene, alkylated azulenes or azulenes substituted at C-1 with electron donating groups (EDG), such as NHAc, OMe or OOCPh, are used.[1] In contrast, the substitution of chlorine by azulenes with electron withdrawing groups (EWG) at the same position occurred in very low yields or even failed. The well known use of pyranylium salts as synthones in the synthesis of pyridines and pyridinium salts suggested the use of such salts for the generation of the corresponding pyridine derivatives. Some (azulen-1-yl)pyridines[2] and (azulen-1-yl)pyridinium salts[3] were already synthesized by us and their properties were reported. The investigation of the peculiarities in the synthesis and properties of 4-azulen-1-yl-pyridines, substituted at C-3 in the azulene moiety with various electron demanding groups, constituted the target of this paper.

Results and Discussion

Pyridine synthesis. The synthetic route to **3** consists of reaction of the 4-(3-substituted azulen-1-yl)-2,6-diphenylpyranylium salts with R = EDG (**2a-c** in Scheme 1 and Table 1) with ammonium acetate in boiling ethanol. However, as shown in Table 1, the good yields in the pyranylium salt preparation step, step (a), are counterbalanced by the moderate efficiency of the subsequent replacement of oxygen by nitrogen, step (b).



1 **2** **3**

R = OMe, OOCPh, NHAc, COOMe, $SO_2PhMe(p)$, NO_2
Symbol = a b c d e f

Scheme 1

Table 1. Synthesis of pyranylium perchlorates, **2**, and subsequent reaction with ammonium acetate (yield of pyridines **3** without starting salt recovery)

Step (a)	Product	**2a**	**2b**	**2c**	**2d**	**2f**
	Yield (%)	44[1]	22[1]	38[1]	10[1]	traces[1]
Step (b)	Product	**3a**	**3b**	**3c**	**3d**	**-**
	Yield (%)	20	55	85	90	-

In contrast, despite the favorable step (b) starting from azulenes with R = EWG, the halogen substitution, step (a), is restrictive. Besides the intrinsic low nucleophilic reactivity of these azulene derivatives, an *ipso* substitution at C-1 in azulene can be observed in the reaction between the halogenated salt and compounds **1d** or **1f**, with the elimination of a methoxycarbonyl or nitro group.[1] Therefore, we have considered the utilization of a catalyst based on palladium chloride for enhancing the coupling reactions between these azulene derivatives and the chloropyranylium salt. However, because both azulene and pyranylium salts are sensitive to the palladium salts only a few references about the palladium catalyzed reactions of these substrates are available. For example, Saito et al.[4] have introduced an acetoxy group into azulene using $Pd(AcO)_2$ and, more recently, Dyker et al.[5] have shown that intermolecular

arylation of unfunctionalized azulene occurred in the presence of a palladium salt catalyst at high temperatures, however only in low yields.[6]

We have examined the reaction of 4-chloro-2,6-diphenylpyranylium perchlorate with azulene derivatives, **1**, in nitromethane, in the presence of a catalytic amount of $PdCl_2$. Under these conditions, 4-azulenylpyranylium salts, **2,** were formed and, without their separation, ammonium acetate was added to the reaction mixture. The pyridines, **3**, were generated *in situ* (Scheme 1) and, to the best of our knowledge, this is the first example in which a pyranylium salt is arylated using a palladium salt as catalyst.

Table 2. Reaction of 4-chloro-2,6-diphenylpyranylium perchlorate with **1**, in the presence of $PdCl_2$ (1% molar) followed by reaction with ammonium acetate, without separation of pyranylium salts **2**

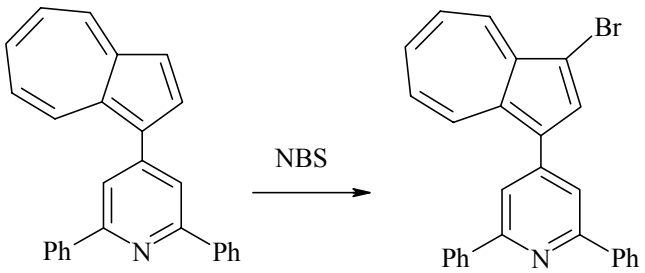
Product	**3c**[*]	**3d**	**3e**	**3f**	**3g**
Yield (%)	63	56[**]	15	15	0

[*]Without $PdCl_2$.. [**]4-(Azulen-1-yl)-2,6-diphenylpyranylium perchlorate was also formed as by product (under 10 %)

As shown in Table 2, starting from methyl 1-azulenecarboxylate, **1d**, 1-nitroazulene, **1f**, or even from 1-(p-tolylsulfonyl)azulene, **1e**, and using $PdCl_2$ as catalyst, acceptable overall yields for steps (a) + (b) were obtained. Under the described reaction conditions, the *ipso* elimination of a substituent during the coupling process was avoided; thus the nitro group was entirely conserved and only a small amount of the compound without CO_2Me was formed. Starting from (azulene-1-yl)-phenyl-diazene, **1g**, the corresponding pyridine was, unfortunately, not generated, possibly because a stable complex was formed between the metal and the azo group.

It is interesting to observe that the protocol for pyridine generation, which avoided the separation of 4-azulenylpyranylium salts as such, was advantageous even for the azulenes with EDG (*e.g.* **1c→3c**); in this instance the catalyst was not necessary.

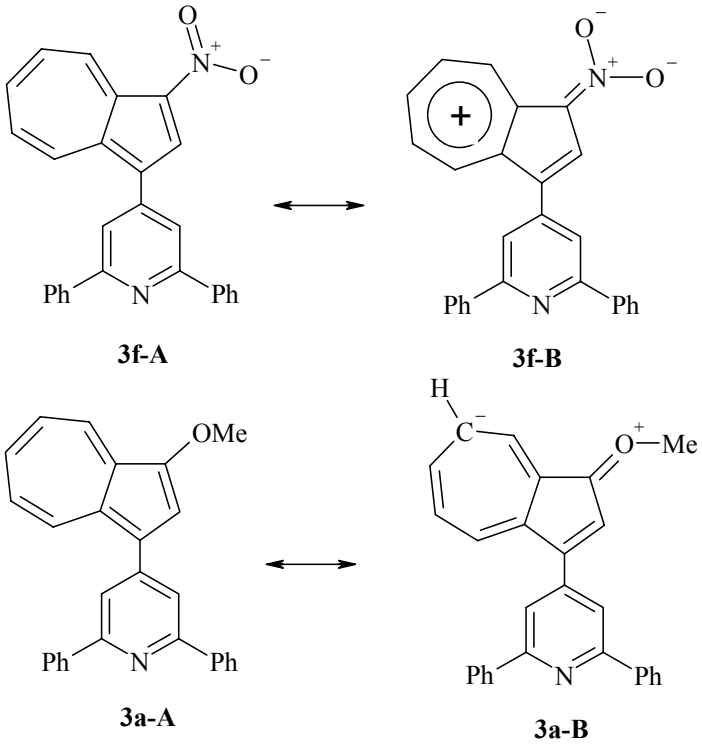
The bromination of compound **3h** with N-bromosuccinimide to 4-(3-bromo-azulen-1-yl)-2,6-diphenylpyridine, **3i**, occurred in good yields (75 %) (Scheme 2). The selectivity of bromination proves that 1-pyridine-substituted azulene, **3h**, still preserves its nucleophilic character at the 3-position. However, nitration at the same position with cupric nitrate in acetic anhydride failed, as did attempted alkylation with methyl iodide at the pyridine nitrogen.



3h **3i**

Scheme 2

Correlation between the pyridine structure and spectra. As expected, the substitution at C-3 in the azulene moiety produces an important effect on the protons belonging to this group by the alteration of electron density. For R = EWG all protons of the seven-membered ring are deshielded (Table 3) due to the charge polarization in azulene, as in contributing structure **3f-B** from Scheme 3. This effect is higher for the 8, 6 and, mainly, the 4 positions. The strong deshielding of the latter proton, as well as of the 2-H, contributes also to the magnetic anisotropy generated by the nitro group at C-3. The higher shielding effect of protons 5-H and 7-H and the slight shielding of the 4, 6 and 8 protons for the compounds with EDG at C-3 result from the charge distribution depicted in Scheme 3, structure **3a-B**. Regarding the ^{13}C-NMR spectra, shown in the experimental part, similar behavior can be observed for the values of the carbon chemical shifts at the azulene moiety. The interruption of continuous conjugation between the substituent R and pyridine produces the loss of its influence on this moiety and also on the phenyl groups (Tables 3 and 4).



Scheme 3

Table 3. ^{1}H-Chemical shifts for 4-(azulen-1-yl)-2,6-diphenylpyridines, **3** (δ in ppm)

Compound	H in azulene						H in	H in phenyls		
	2	4	5	6	7	8	Py	2,6	3,5	4
3a	7.61	8.33	6.90	7.45	6.92	8.46	7.89	8.22	7.52	7.44
3b	8.25	8.41	7.17	7.65	7.19	8.64	7.93	8.22	7.57	7.52
3c	8.51	8.14	7.10	7.60	7.13	8.55	7.87	8.20	7.52	7.44
3i	8.11	8.46	7.28	7.71	7.34	8.60	7.87	8.23	7.54	7.47
3h	8.18	8.44	7.28	7.72	7.29	8.71	7.95	8.25	7.54	7.45
3d	8.62	9.78	7.67	8.22	7.54	8.78	7.91	8.23	7.52	7.44
3f	8.71	9.90	7.88	8.08	7.74	8.86	7.87	8.22	7.54	7.47

It is interesting to underline that the azulene substitution by either EWG or EDG induces a bathochromic effect in the UV-Vis spectra (Table 4) due to the advanced charge polarization of the azulene system in the ground state. This might be also the explanation for the absence of solvatochromism in the studied compounds.

Table 4. UV-Vis spectra of 4-(azulen-1-yl)-2,6-diphenylpyridines, **3** (in MeOH); $\lambda_{max}/\varepsilon$

Compound	L1	L2	L3	L4	L5
3a	220/4.46	246/4.55	285/4.45	308/4.29 sh, 335/3.95sh	402/3.90
3b	217/4.42	244/4.57	285/4.45	303/4.49 sh	375/3.94
3c	216/4.31	246/4.51	294/4.47	-	385/3.79
3i	219/4.37	245/4.47	286/4.40	-	374/3.88
3h	217/4.46	243/4.53	279/4.46	300/4.40, 313/4.32 sh	370/3.93
3e	220/4.32	240/4.37	296/4.42	-	365/3.77
3d	-	240/4.45	293/4.48	-	374/3.72
3f	219/4.36	233/4.37	308/4.34	-	403/3.68

The presented results are in accord with our supposition that the electron demand of the C-3 substituent of azulene in (4-azulen-1-yl)-pyridines induces considerable differences, both for synthesis and for the spectral properties of these compounds.

Experimental Section

General Procedures. Melting points: Kofler apparatus (Reichert Austria). Elemental analyses: Perkin Elmer CHN 240B. ^{1}H- and ^{13}C-NMR: Bruker Avance DRX4 (^{1}H: 400 MHz, ^{13}C: 100.62 MHz), *J* values are given in Hz, TMS was used as internal standard in $CDCl_3$ or DMSO-d_6 as solvent; COSY and HETCOR correlation experiments were used for the structure assignment. UV-Vis spectra in methanol: Specord UV-Vis spectrometer (C. Zeiss Jena). Mass spectra: JEOL JMS-DX303 spectrometer coupled to analytical gas-chromatograph Shimadzu GC-14B with a DB-1 capillary column and C-R6A integrator and Finnigan MAT 311-A/100 MS; for the spectral recording in the solid state a Carlo Erba QMD 1000 (EI+, 70 eV) device was used. Column chromatography: silica gel [70-230 mesh (ASTM)]. The pyranylium salts 4-substituted with azulene or chlorine were obtained as described in our previous paper.[1] The numbering for the positions in the pyridines characterized below were presented in Scheme 1. The nomenclature was obtained by use of the ACD/I-Lab web service (ACD/IUPAC Name Free 7.06).

Experimental procedures

Preparation of pyridines. (a) From pyranylium salts. To a solution of 2,6-diphenyl-4-(3-substituted-azulen-1-yl)-pyranylium perchlorate **2R** (1 mmol) in ethanol, ammonium acetate (10 eq) was added and the solution was magnetically stirred and refluxed for 1 hour. The alcohol was evaporated in vacuo and the residue was separated by column chromatography on silica gel using chloroform as eluent. The pyridine was collected as the first colored fraction due to the lower polarity of pyridines as compared with the other products (with unknown structure) in the reaction mixture. The pyridine migrated as a brown band on the column, however the solution was generally green.

(b) From 4-chloro-2,6-diphenyl-pyranylium perchlorate. A magnetically stirred mixture containing azulenic compound **1R** (1 mmol) and 2,6-diphenyl-4-chloropyranylium perchlorate (1 mmol) in nitromethane (10 ml) was heated at 100 °C for one hour and cooled to room temperature. When $PdCl_2$ (1% molar) was used as catalyst (starting from **2d**, **2e** and **2f**) the reaction time was prolonged to 4 hours. Ammonium acetate (10 eq) was then added and the reflux was continued for one hour. The nitromethane was evaporated in vacuum and the resulting mixture was worked-up as above.

For the experiments, which occurred with substituent elimination (such as, starting from **1d**), some difficulties were encountered with the separation of pyridines by column chromatography. These difficulties were surpassed if the reaction mixture was brominated with NBS (1 eq). The **3h** brominated product **3i** was conveniently separated by column chromatography from the other pyridine derivatives (**3d, 3e and 3f),** which do not react with NBS at room temperature.

Compound characterization

4-(3-Methoxy-azulen-1-yl)-2,6-diphenylpyridine (**3a)**. Green oil. UV-Vis (MeOH), λ_{max}, (log ε): 220 (4.46), 246 (4.55), 285 (4.45), 308 (4.29), 335 (3.95) sh, 402 (3.90). ^{1}H-NMR ($CDCl_3$): 4.11 (s, 3 H, CH_3O), 6.90 (t, ^3J = 9.4 Hz, 1 H, 5'-H), 6.92 (t, ^3J = 9.8 Hz, 1 H, 7'-H), 7.44 (t, ^3J = 7.2 Hz, 2 H, 4"-H), 7.45 (t, ^3J = 9.8 Hz, 1 H, 6'-H), 7.52 (t, ^3J = 7.7 Hz, 4 H, 3"-H, 5"-H), 7.61 (s, 1 H, 2'-H), 7.89 (s, 2 H, 3-H, 5-H), 8.22 (d, ^3J = 7.1 Hz, 4 H, 2"-H, 6"-H), 8.33 (d, ^3J = 9.2 Hz, 1 H, 4'-H), 8.46 (d, ^3J = 9.7 Hz, 1 H, 8'-H). ^{13}C-NMR ($CDCl_3$): 58.08 (CH_3O), 116.6 (C2'), 119.4 (C3, C5), 121.4 (C7'), 122.2 (C5'), 123.9 (C3'), 127.2 (C2", C6"), 127.5 (C3a'), 128.7 (C3", C5"), 129.0 (C4"), 129.6 (C8a'), 134.0 (C4'), 136.4 (C8'), 139.8 (C1"), 140.2 (C6'), 146.4 (C1'), 149.7 (C4), 157.2 (C2, C6). MS (70 eV, m/z): 388 (26), 387 [M^+, 100], 373 (26), 372 (99), 239 (31), 171 (29), 77 (32). Calculated for $C_{28}H_{21}NO$: C, 86.79; H, 5.46; N 3.61, found C, 86.78; H, 5.48; N 3.60.

3-(2,6-Diphenylpyridin-4-yl)-azulen-1-yl-benzoate (**3b).** green crystals, m. p. 137-8 °C. UV-Vis (MeOH), λ_{max}, (log ε): 217 (4.42), 244 (4.57), 285 (4.45), 303 sh (4.49), 375 (3.94). ^{1}H-NMR ($CDCl_3$): 7.17 (t, ^3J = 9.8 Hz, 1 H, 5'-H), 7.19 (t, ^3J = 9.8 Hz, 1 H, 7'-H), 7.42 (t, ^3J = 7.2 Hz, 2 H, 3"'-H, 5"'-H), 7.52 (t, ^3J = 7.2 Hz, 2 H, 4"-H), 7.65 (t, ^3J = 10.0 Hz, 1 H, 6'-H), 7.57 (t, ^3J = 7.6 Hz, 4 H, 3"-H, 5"-H), 7.68 (t, ^3J = 7.6 Hz, 1 H, 4"'-H), 7.93 (s, 2 H, 3-H, 5-H), 8.22 (d, ^3J = 7.2 Hz, 4 H, 2"-H, 6"-H), 8.25 (s, 1 H, 2'-H), 8.35 (d, ^3J = 8.0 Hz, 2 H, 2"'-H, 6"'-H), 8.41 (d, ^3J = 9.6 Hz, 1 H, 4'-H), 8.65 (d, ^3J = 9.6 Hz, 1 H, 8'-H). ^{13}C-NMR ($CDCl_3$): 119.7 (C3, C5), 123.2 (C5'), 124.4 (C7'), 124.8 (C1'), 127.2 (C2", C6"), 127.5 (C2'), 128.7 (C3", C5"), 128.8 (C3"',C5"'), 129.0 (C1"', C4"), 129.4 (C8a'), 130.2 (C2"', C6"'), 131.5 (C3a'), 133.4 (C4'), 133.8 (C4"'), 136.7 (C8'), 138.0 (C3'), 139.7 (C1"), 140.0 (C6'), 145.8 (C4), 157.2 (C2, C6), 164.8 (CO). MS (70 e(V, m/z): 478 (22), 477 [M^+, 62], 373 (23), 372 (48), 239 (28), 105 (98), 77 (100). Calculated for $C_{34}H_{24}NO$: C, 88.28; H, 5.23; N 3.03, found C, 88.24; H, 5.26; N 3.55.

4-(3-Acetylamino-azulen-1-yl)-2,6-diphenylpyridine (3c). Blue crystals, m. p. 251 °C. UV-Vis (MeOH), λ_{max}, (log ε): 216 (4.31), 246 (4.51), 294 (4.47), 385 (3.79). ^{1}H-NMR ($CDCl_3$): 2.34 (s, 3 H, CH_3), 7.10 (t, ^3J = 9.2 Hz, 1 H, 5'-H), 7.13 (t, ^3J = 10.0 Hz, 1 H, 7'-H), 7.44 (t, ^3J = 7.2 Hz,

2 H, 4”-H), 7.52 (t, ^3J = 7.4 Hz, 4 H, 3”-H, 5”-H), 7.60 (t, ^3J = 10.0 Hz, 1 H, 6’-H), 7.69 (bs, 1 H, NH), 7.87 (s, 2 H, 3-H, 5-H), 8.14 (d, ^3J = 9.6 Hz, 1 H, 4’-H), 8.20 (d, ^3J = 7.2 Hz, 4 H, 2”-H, 6”-H), 8.51 (s, 1 H, 2’-H), 8.55 (d, ^3J = 9.2 Hz, 1 H, 8’-H). ^{13}C-NMR (DMSO-d_6): 23.20 (Me), 118.9 (C3, C5), 122.1 (C5’), 124.1 (C7’), 124.7 (C1’), 126.2 (C3’), 126.8 (C2”, C6”), 128.6 (C3”, C5”), 129.0 (C4”), 129.2 (C3a’), 130.0 (C2’), 131.7 (C8a’), 133.9 (C4’), 135.8 (C8’), 138.8 (C1”), 139.9 (C6’), 145.8 (C4), 156.1 (C2, C6), 168.0 (CO). MS (70 eV,m/z): 416 (13), 414 [M^+, 100], 373 (43), 371 (63), 43 (87). Calculated for $C_{29}H_{22}N_2O$: C, 84.03; H, 5.35; N 6.76, found C, 84.00; H, 5.37; N 6.71.

4-(3-Methoxycarbonyl-azulen-1-yl)-2,6-diphenylpyridine (3d). Violet crystals, m. p. 150 ^{o}C. UV-Vis (MeOH), λ_{max}, (log ε): 240 (4.45), 293 (4.48), 374 (3.72). ^{1}H-NMR ($CDCl_3$): 4.01 (s, 3 H, CH_3O), 7.46 (t, ^3J = 7.2 Hz, 2 H, 4”-H), 7.53 (t, ^3J = 7.7 Hz, 4 H, 3”-H, 5”-H), 7.54 (t, ^3J = 9.8 Hz, 1 H, 7’-H), 7.64 (t, ^3J = 10.0 Hz, 1 H, 5’-H), 7.90 (t, ^3J = 10.0 Hz, 1 H, 6’-H), 7.91 (s, 2 H, 3-H, 5-H), 8.22 (d, ^3J = 7.2 Hz, 4 H, 2”-H, 6”-H), 8.62 (s, 1 H, 2’-H), 8.78 (d, ^3J = 10.0 Hz, 1 H, 8’-H), 9.78 (d, ^3J = 10.0 Hz, 1 H, 4’-H). ^{13}C-NMR ($CDCl_3$): 51.36 (CH_3O), 116.4 (C3’), 119.6 (C3, C5), 127.2 (C2”, C6”), 128.0 (C7’), 128.8 (C3”, C5”), 129.0 (C5’, C4”), 129.2 (C1’), 136.8 (C8’), 138.9 (C4’), 139.5 (C1”), 140.1 (C2’), 140.3 (C6’), 140.4 (C3a’), 142.3 (C8a’), 145.9 (C4), 157.4 (C2, C6), 165.6 (CO). MS (70 eV,m/z): 417 (13), 415 [M^+, 100], 384 (21), 356 (26), 277 (20), 77 (33). Calculated for $C_{29}H_{21}NO_2$: C, 83.93; H, 5.09; N 3.37, found C, 83.89; H, 5.13; N 3.36.

4-(3-(p-Tolylsulfonyl)-azulen-1-yl)-2,6-diphenylpyridine (3e). violet crystals, m. p. 108 ^{o}C. UV-Vis (MeOH), λ_{max}, (log ε): 220 (4.32), 240 (4.37), 296 (4.42), 365 (3.77). ^{1}H-NMR ($CDCl_3$): 2.36 (s, 3 H, CH_3), 7.27 (d, ^3J = 8.0 Hz, 2 H, 3”’-H, 5”’-H), 7.46 (tt, ^3J = 7.2 Hz, ^4J =1.2 Hz, 2 H, 4”-H), 7.53 (tt, ^3J = 7.7 Hz, ^4J = 1.6 Hz, 4 H, 3”-H, 5”-H), 7.57 (t, ^3J = 9.6 Hz, 1 H, 7’-H), 7.67 (t, ^3J = 9.8 Hz, 1 H, 5’-H), 7.86 (s, 2 H, 3-H, 5-H), 7.95 (d, ^3J = 8.4 Hz, 2 H, 2”’-H, 6”’-H), 7.96 (t, ^3J = 9.8 Hz, 1 H, 6’-H), 8.21 (dt, ^3J = 6.8 Hz, ^4J = 1.2 Hz, 4 H, 2”-H, 6”-H), 8.56 (s, 1 H, 2’-H), 8.79 (d, ^3J = 9.6 Hz, 1 H, 8’-H), 9.44 (d, ^3J = 9.6 Hz, 1 H, 4’-H). ^{13}C-NMR ($CDCl_3$): 21.51 (CH_3), 119.5 (C3, C5), 124.5 (C1’), 126.8 (C2”’, C6”’), 127.2 (C2”, C6”), 128.2 (C3’), 128.6 (C1”), 128.8 (C3”, C5”), 129.2 (C4”), 129.8 (C3”’, C5”’), 137.7 (C8’), 138.1 (C4’), 138.5 (C3a’), 138.6 (C2’), 139.3 (C7’), 140.0 (C8a’), 141.0 (C5’), 141.2 (C6’), 143.5 (C4”’), 145.0 (C1”’), 157.5 (C2, C4, C6). MS (ESI, m/z): 512 [M^++1, 100]. Calculated for $C_{34}H_{25}NSO_2$: C, 79.82; H, 4.93; N, 2.74; found C, 79.65; H, 4.99; N 2.59.

4-(3-Nitro-azulen-1-yl)-2,6-diphenylpyridine (3f). Brown crystals, m.p. 194 ^{o}C. UV-Vis (MeOH), λ_{max}, (log ε): 219 (4.36), 233 (4.37), 308 (4.34), 403 (3.68). ^{1}H-NMR ($CDCl_3$): 7.74 (t, ^3J = 9.6 Hz, 1 H, 5’-H), 7.88 (t, ^3J = 10.0 Hz, 1 H, 7’-H), 7.47 (t, ^3J = 7.2 Hz, 2 H, 4”-H), 7.54 (t, ^3J = 7.8 Hz, 4 H, 3”-H, 5”-H), 8.08 (t, ^3J = 10.0 Hz, 1 H, 6’-H), 7.87 (s, 2 H, 3-H, 5-H), 8.72 (s, 1 H, 2’-H), 8.22 (d, ^3J = 7.6 Hz, 4 H, 2”-H, 6”-H), 8.46 (d, ^3J = 10.0 Hz, 1 H, 8’-H), 9.90 (d, ^3J = 10.0 Hz, 1 H, 4’-H). ^{13}C-NMR ($CDCl_3$): 134.1 (C3’), 1195 (C3, C5), 134.8 (C5’), 134.2 (C7’), 127.1 (C2”, C6”), 127.6 (C1’), 128.8 (C3”, C5”), 129.3 (C4”), 134.8 (C3a’), 139.0 (C8’), 139.2 (C4’), 138.9 (C8a’), 134.2 (C2’), 139.8 (C1”), 142.2 (C6’), 144.3 (C4), 157.6 (C2, C6). MS (ESI

,m/z): 403 [M^++1, 100]. Calculated for $C_{27}H_{18}N_2O_2$: C, 80.58; H, 4.51; N 6.96, found C, 80.54; H, 4.43; N 6.87.

4-(3-Bromo-azulen-1-yl)-2,6-diphenylpyridine (3i), Blue-green oil. UV-Vis (MeOH), λ_{max}, (log ε): 219 (4.37), 245 (4.47), 286 (4.40), 374 (3.88). ^{1}H-NMR ($CDCl_3$): 7.28 (t, ^3J = 9.8 Hz, 1 H, 5'-H), 7.34 (t, ^3J = 9.8 Hz, 1 H, 7'-H), 7.47 (t, ^3J = 7.2 Hz, 2 H, 4"-H), 7.54 (t, ^3J = 7.8 Hz, 4 H, 3"-H, 5"-H), 7.71 (t, ^3J = 10.0 Hz, 1 H, 6'-H), 7.87 (s, 2 H, 3-H, 5-H), 8.11 (s, 1 H, 2'-H), 8.23 (d, ^3J = 7.2 Hz, 4 H, 2"-H, 6"-H), 8.46 (d, ^3J = 9.6 Hz, 1 H, 4'-H), 8.60 (d, ^3J = 9.6 Hz, 1 H, 8'-H). ^{13}C-NMR ($CDCl_3$): 104.7 (C3'), 119.4 (C3, C5), 125.1 (C5'), 124.5 (C7'), 127.1 (C2", C6"), 127.8 (C1'), 128.7 (C3", C5"), 129.0 (C4"), 135.8 (C3a'), 135.9 (C8'), 137.2 (C4'), 137.3 (C8a'), 137.6 (C2'), 139.6 (C1"), 140.0 (C6'), 145.3 (C4), 157.3 (C2, C6). MS (70 eV,m/z): 437 (100), 435 [M^+, 100], 357 (20), 277 (38), 77 (23). Calculated for $C_{27}H_{19}BrN$: C, 74.15; H, 4.38; N 3.20; Br 18.27, found C, 74.12; H, 4.40; N 3.22; Br 18.26.

Acknowledgements

The Ministry of Education and Research, Romania, provided a part of the financial support in the frame of Excellency Research Program nr. CEx 05-D11-20/2005. We are grateful to Dr. Filip Chiraleu for recording UV-Vis spectra.

References and Footnotes

1. 1 Razus, A. C.; Birzan, L.; Pavel, C.; Lehadus, O.; Corbu, A. C.; Enache, C. *J. Het. Chem.* accepted **2006**.
2. Razus, A. C. ; Birzan, L.; Pavel, C.; Lehadus, O.; Corbu, A.; Chiraleu, F.; Enache, C. *J. Het. Chem*. submitted. The paper reports the pyridines with azulene moiety substituted only by alkyl groups.
3. Razus, . A. C.; Birzan, L.; Pavel, C.; Lehadus, O.; Corbu, A.; Chiraleu, F.; Enache, C. *J. Het. Chem*. submitted.
4. Saito, K.; Kozaki, M.; Uenishi, K.; Abe, N.; Takahashi, K. *Chem. Pharm. Bull.* 1991 **39**, 1843 .
5. G. Dyker, S. Borowski, J. Heiermann, J. Korning, K. Opwis, G. Henkel and M. Kockerling, J. Organometallic Chem., **606**, 108 (2000).
6. While azulene can easily be arylated with active haloaryls, such as picryl chloride or *sim*-trichlorotriazene, it can not interact with normal haloaryls.