CONVERSIONS OF 9-CHLORO-4-AZAFLUORENE TO AZALENES

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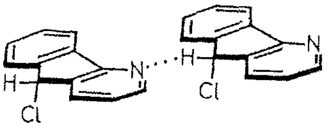
The iodomethylate of 9-chloro-4-azafluorene is converted to 1H-1-methyl-indeno[1,2-b]pyridine when treated with base. We discuss the structure of compounds containing azalene fragments, which are formed upon heating 9-chloro-4-azafluorene. We discuss some considerations concerning the nomenclature of azulenes with the azafluorene skeleton.

The major method for obtaining azalenes is base treatment of quaternary salts of condensed polynuclear compounds which are classified as CH-acids and contain the pyridinium ring [1]. Continuing investigations of azalenes obtained by this route from quaternary salts of azafluorenes, we turned to synthesis of pseudoazulenes based on 9-chloro-4-azafluorene (I), which is obtained in quantitative yield upon reaction of 4-azafluorenol-9 with thionyl chloride at room temperature. In the IR spectrum of chloride I, there is an absorption band for the stretching vibrations of the C–Cl bond at 690 cm^{-1}. According to data in [2], we can hypothesize that this bond is axial. Partial confirmation of such a hypothesis comes from comparison of the IR spectra of 4-azafluorene and chloride I. In the IR spectrum of compound I, the stretching vibrations of the $C_{(9)}-H$ bond appear at 2955 cm^{-1}, and in the spectrum of 4-azafluorene the bending vibrational band for this bond is shifted toward the 1410 cm^{-1} region, probably due to the axial orientation of the chlorine atom.



9-Chloro-4-azafluorene exists in solution in the form of intermolecular associates, in which the hydrogen at the 9 position of one of its molecules interacts with the nitrogen atom of the other molecule. Such a conclusion is drawn on the basis of comparison of the electronic absorption spectra of chloride I and 4-azafluorene. In the spectrum of chloride I, we observe three bands characteristic for aromatic systems with λ_{max} 210-224 (β-band), 285 (p-band), and 300-312 nm (α-band). Compared with the electronic absorption spectra of 4-azafluorene, the p-band in the spectrum of chloride I experiences a 30 nm bathochromic shift, and the intensity of the α-band in the spectrum of 4-azafluorene is reduced compared with the intensity of the same band in the spectrum of chloride I; this, as we assume, is due to the existence of 9-chloro-4-azafluorene in the form of the associates indicated above. We need to also take into account the relatively elevated CH-acidity of compound I, containing the pyridinium nitrogen atom.

From compound I, we obtained a quaternary salt: 4-methyl-9-chloro-4-azafluorenium iodide (II). Treating this salt with potassium hydroxide in the presence of water and chloroform, we obtained in almost the theoretical yield 1H-1-methylindeno[1,2-*b*]pyridine (4H-4-methyl-4-azafluorene) (III), synthesized earlier by the same route from 4-azafluorene iodomethylate [3]. Thus in the conversion of the iodomethylate II to azalene, cleavage of the chlorine atom rather than the hydrogen atom from the 9 position occurs, and the possible 1H-1-methyl-5-chloroindeno[1,2-*b*]pyridine is not formed. We must

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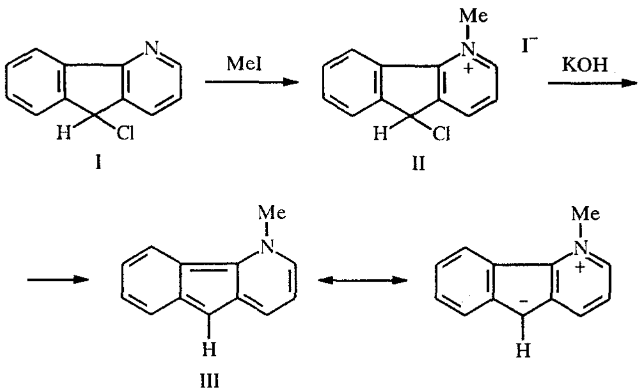
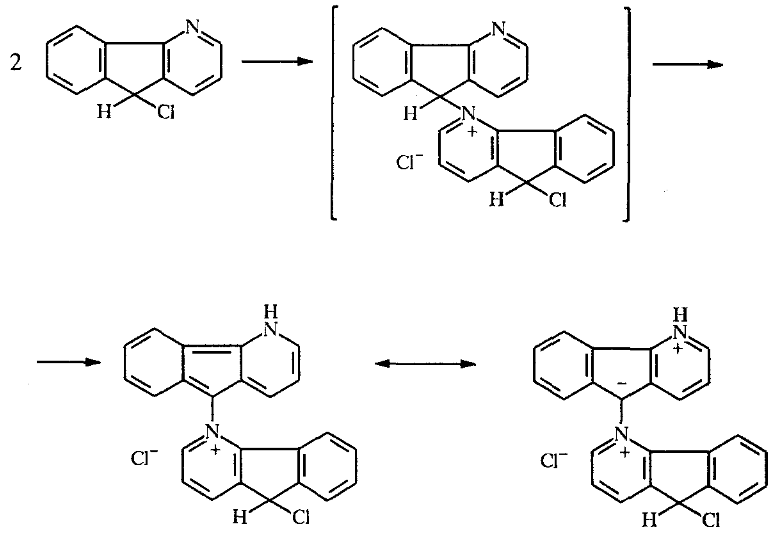
note that in the mass spectrum of chloride I, there is a fragment corresponding to elimination of the chlorine atom: (M−Cl)+ with *m/z* 166 (100%).

The azalene III forms almost black crystals. Its solution in chloroform is dark blue, and its solution in ethanol is reddish violet. In its electronic absorption spectrum, there is an absorption band with λ_{max} 530 nm, which is characteristic for pseudoazulenes [4].



Taking into account the presence in compound I of the chlorine atom and the pyridinium nitrogen atom, we can assume that upon intermolecular interaction of this chlorine, a quaternary salt will be formed with two azafluorene fragments. Accordingly, we studied the conversion of compound I when it is heated.

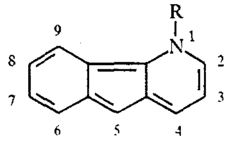
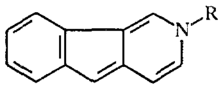
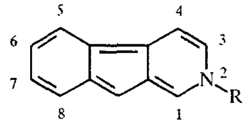
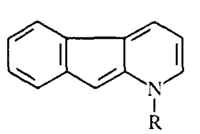


IV

When held for 2 h at 80°C, the color of crystals of 9-chloro-4-azafluorene (which was light yellow, T_{mp} 103-104.5°C) sharply changes. As a result, dark-green crystals are formed which soften and melt within the range 150-200°C. In the electronic absorption spectra, we observe absorption bands in the visible region with λ_{max} 600 (log ε 2.16 and λ_{max} 427 nm (log ε 2.77), which are not observed in the spectrum of the original chloride I. Probably upon moderate heating a reaction occurs between two molecules of 9-chloro-4-azafluorene and a quaternary salt is formed: N-(4-azafluoren-9-yl)-9-chloro-4-azafluorenium chloride, the N-azafluorenium fragment of which is rearranged to azalene. Evidence for this comes from the spectral data presented above, which are characteristic for azalenes, and also the appearance of a deep color. Probably the dark-green crystals have the structure of 9-chloro-N-[1H-indeno[1,2-*b*]pyridine-5-yl]-4-azafluorenium chloride (IV).

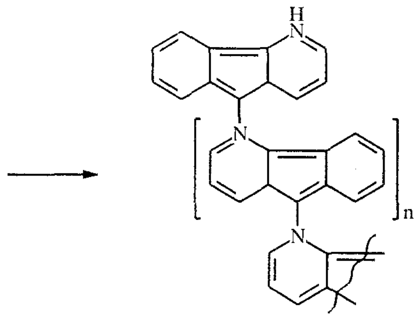
Upon heating compound IV for 1-3 h at ≈150°C, the color deepens to black. This is probably connected with further condensation and formation of a polymer-like compound V (T_{mp} > 280°C) with azalene fragments in a chain.

TABLE 1

Azalene	Common name	Recommended name
	1H-1R-indeno[1,2-b]-pyridine	1H-1-R-indeno(1H) [1,2-b]pyridylidene-2
	2H-2-R-indeno[1,2-c]-pyridine	2H-2-R-indeno[1,2,c]-pyridylidene-4
	2H-2-R-indeno[2,1-c]-pyridine	2H-2-R-indeno(2H) [2,1-c]pyridylidene-4
	1H-1-R-indeno[2,1-b]-pyridine	1H-1-R-indeno[2,1-b]-pyridylidene-2

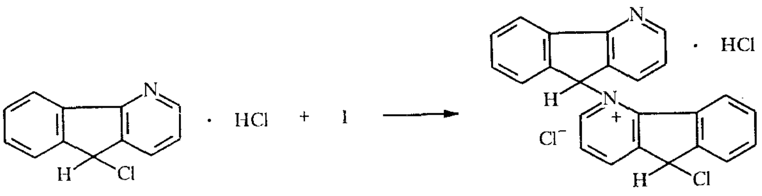
Notes. The following names can probably be validly used for the azulenes presented in the table (top to bottom): 4H-4-R-4-azafluorene, 3H-3-R-3-azafluorene, 2H-2-R-2-azafluorene, and 1H-1-R-1-azafluorene. Considering the shortness of these names, they might be more acceptable.

IV



V

Indirect confirmation of the possible route for formation of compound V may be the fact that upon heating 9-chloro-4-azafluorene hydrochloride (VI) without a solvent, in contrast to the free base I, such changes do not occur. But upon heating equimolecular amounts of hydrochloride VI and 9-chloro-4-azafluorene (I) in ethanol, 9-(9-chloro-4-azafluorenium chloride-4-yl)-4-azafluorene hydrochloride (VII) is formed in quantitative yield, isolated as orange crystals. The IR spectrum of compound VII is identical to the spectrum of the hydrochloride VI.

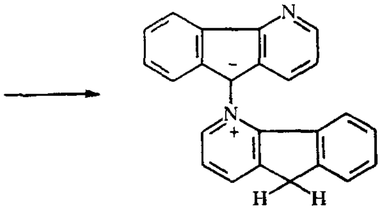


VI

VII

Upon treatment of the salt VII with sodium borohydride, we obtain a light-yellow material in quantitative yield. In its electronic absorption spectrum, there is no band with λ_{max} in the interval 400-600 nm, characteristic for azalenes, which together with the absence of a deep coloring suggests that there is no pseudoazulene fragment in its molecule. Probably under the influence of sodium borohydride, reduction of the chloromethylene group at the 9′ position and cleavage of two hydrogen chloride molecules occur, as a result of which the 4-azafluorenium-(4-azafluoren-4-yl) ylide (VIII) is formed.

VII



VIII

In the mass spectrum of compound VIII, there is a molecular ion peak with *m/z* 332 (100%). The band of medium intensity at 3070 cm^{-1} in its IR spectrum belongs to vibrations of the methylene group. A characteristic feature of the IR spectrum is the enhanced intensity (doubling) of the absorption band for vibrations at 1600 and 1580 cm^{-1}, which suggests a low-frequency shift of the $\nu_{C...N}$ band in the ylides. The observed absorption bands in the electronic absorption spectra are similar to the spectrum of 4-azafluorene in both position and configuration, except for the fact that in the long-wavelength fall-off of the α-band with λ_{max} 312 (log ε 4.64) we note a shoulder with λ_{max} ~325 nm (log 3.74), similar to that which is observed in the spectrum of the starting compound VII. The yellow color of the solution of ylide VIII in ethanol changes to dark green upon addition of base. In this case, in the electronic absorption spectrum we observe bands with λ_{max} 650 and 460 nm, which are observed in the electronic absorption spectrum upon treatment of a solution of 9-chloro-4-azafluorene iodomethylate (II) with a solution of potassium hydroxide. This is probably connected with conversion of two azafluorene fragments of compound VIII to azalenes. However, we could not isolate such a possible uncondensed diazalene, similar to the analogous condensed system we described earlier [5].

Compounds III and IV are named according to rules in the fundamental review devoted to pseudoazulenes [1]. We considered it to be expedient to discuss some consideration concerning the nomenclature of azalenes obtained from azafluorenes. This is partially connected with the fact that in [1] citations to our work are given. Azalenes, whose structure is similar to azafluorenes, are called H-indeopyridines. Such a name probably does not accurately reflect their structure.

We must note that in their molecules there is no "pyridinium" ring. The nitrogen-containing fragment in their molecules has the structure of pyridone rings. This fragment in azalenes in this series which are isomers with respect to the position of the nitrogen atom is represented as pyridylidene-2(1H) and pyridylindene-4(1H). Such a name for these fragments is analogous to the name for the divalent radical formed from 1,2-dihydronaphthalene: naphthalidene-2(1H) [6]. We need to also consider a second fact. In isomeric azalenes in this series, two types of indene fragments are condensed with the nitrogen-containing ring: 1H- and 2H-indene. In Table 1, we present the common names and the correct names (in our opinion) for isomeric azalenes with the azafluorene skeleton.

EXPERIMENTAL

The IR spectra were recorded on the UR-20 spectrophotometer in KBr disks. The electronic absorption spectra were obtained on the Specord UV-Vis spectrophotometer in ethanol. The molecular masses were determined by mass spectrometry on the MKh-1303 mass spectrometer with ionizing electron energy of 70 eV.

The elemental analysis data for compounds I-VIII correspond to the calculated values.

9-Chloro-4-azafluorene (I, $C_{12}H_8ClN$). A. Allow the following to react: 0.55 g (3 millimoles) 4-azafluorenol, 20 ml benzene, and 1.7 g (14 millimoles) thionyl chloride. Hold at 20°C for 1 h. Distill off the benzene and the thionyl chloride. Treat the residue with a sodium carbonate solution up to pH 9. Extract with ether. From the residue, after distillation of the ether we chromatographically isolated 0.5 g (83%) of compound I; light-yellow crystals, T_{mp} 103-104.5°C (from hexane). M^+ 201, 203.

B. Analogous procedure, without using benzene. Chloride I was obtained in 76% yield.

Hydrochloride of compound I, T_{mp} 208-211°C.

Iodomethylate II, black crystals, T_{mp} 178-180°C (from ethanol).

1H-1-methylindeno[1,2-*b*]pyridine (1H-1-methylindeno(2H)[1,2-*b*]pyridylidene-2) (III, $C_{13}H_{11}N$). Gradually add with stirring powdered potassium hydroxide to a mixture of 0.5 g (1.46 millimoles) iodomethylate II, 20 ml water, and 20 ml chloroform until an intense dark-blue color appears. From the chloroform solution, we isolated 0.25 g (96%) of the azalene III; dark crystals, T_{mp} 187-189°C (with decomposition) [7] M^+ 181.

9-Chloro-N-[1H-indeno-[1,2-*b*]pyridine-5-yl]-4-azafluorenium Chloride (IV, $C_{24}H_{16}N_2Cl_2$). Hold for 2 h at 80°C 1.5 g (7.5 millimoles) chloride I. After cooling, wash the crystalline residue twice with hot hexane (10 ml). We isolated 0.8 g (53%) compound IV; dark-green crystals, T_{mp} 150-200°C (with decomposition). Heat 0.3 g (1.49 millimoles) compound IV at ≈150°C for 1 h. Grind the residue in ether. We obtained 0.2 g (74%) of substance V in the form of a black powder, which begins to melt with decomposition at ≈280°C.

9-(9-chloro-4-azafluorenium Chloride-4-yl)-4-Azafluorene Hydrochloride (VII, $C_{24}N_2H_{17}Cl_3$). Boil for 6 h 0.5 g (2.48 millimoles) chloride I and 0.59 g (2.48 millimoles) of its hydrochloride VI in 25 ml absolute ethanol. Distill off the alcohol. Grind the residue in absolute ether. We isolated 1.03 g (95%) of compound VII; orange crystals, T_{mp} 268-270°C.

4-Azafluorenium-(4-azafluoren-4-yl) Ylide (VIII, $C_{24}H_{17}N_2$). Boil a solution of 0.6 g (1.4 millimoles) compound VII in 30 ml ethanol and 1 g (26.3 millimoles) sodium borohydride with stirring for 2 h. Add 5 ml water. Extract with ether, dry with potash. From the ether extract we isolated 0.38 g (85%) compound VIII; light-yellow crystals, T_{mp} 213-215°C.

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