REACTION OF 9-HYDROXY(CHLORO, BROMO)-4-AZAFLUORENE TO BIS[9-CHLORO(BROMO-4-AZA-FLUOREN-9-YL]

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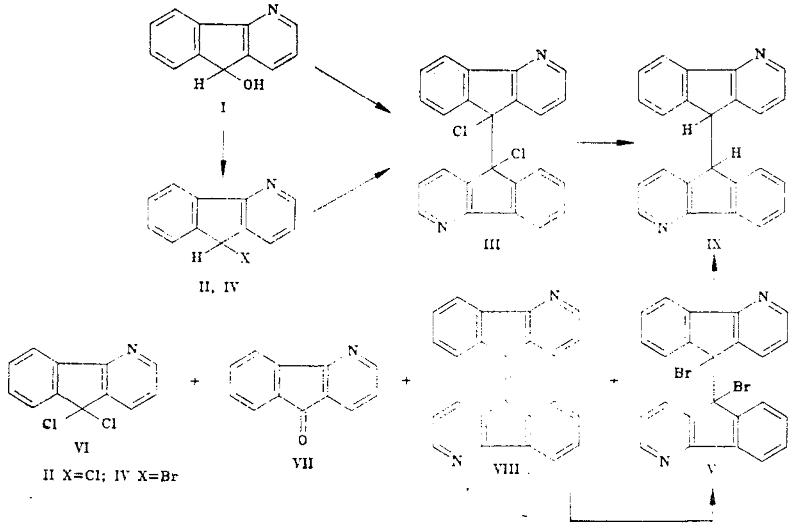
4-Aza-fluoren-9-ol and 9-chloro(bromo)-4-azafluorenes are converted in high yields upon refluxing with thionyl chloride to form bis[9-chloro(bromo)-4-azafluoren-9-yl]. At about 20°C, azafluorenol and thionyl chloride form 9-chloro-4-azafluorene. Mechanisms are proposed for these reactions.

Treatment of 4-azafluoren-9-ol (I) with thionyl chloride at 20°C in benzene or in the absence of solvent gave 9-chloro-4-aza-fluorene (II) in quantitative yields. Evidently this reaction occurs predominantly via an SN_1 mechanism.

A different reaction of I with thionyl chloride occurs upon heating and the basic product is bis[9-chloro-4-azafluoren-9-yl] (III) in 76.7% yield. The dichloride III is also formed from compound II upon refluxing with thionyl chloride in 87% yield. It seems likely that the azafluorene II is an intermediate in the conversion of I to the dimer III. Apparently reaction of the comparatively powerful CH-acid II with thionyl chloride forms bis[9-chloro-4-azafluoren-9-yl]sulfoxide which is oxidized by atmospheric oxygen to sulfur dioxide and 9-chloro-4-azafluoren-9-yl radicals, the recombination of which leads to compound III. A similar conversion of 9-formylfluorene to bis[9-formylfluoren-9-yl] has also been prepared [2] by heating fluorene with phosphorus pentachloride at 190°C.



These reactions take place with the formation of common intermediate stages and compositions as evidenced by the formation of bis[9-bromo-4-azafluoren-9-vl] (V) when (IV) is heated with thionyl chloride in benzene. In this case the reaction gave not only the dibromide V in 50% yield but also a mixture of 9,9-dichloro-4-aza-fluorene (VI) and 4-azafluoren-9-one (VII). When this reaction is carried out without solvent V is formed in 20% yield together with VI (54%) and di(4-azafluoren-9-ylidene) (VIII) (23%). A carbene mechanism for the formation of VIII has been discussed in [3]. The dibromide V was obtained by bromination of VIII.

Heating of dichloride III and also dibromide V with zinc dust in absolute ethanol gave bis[4-azafluoren-9-yl] (IX). In this case VII is not formed, evidently due to the more

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favorable transoid orientation of halogen atoms with steric hindrance to system change in the cisoid conformation.

In the PMR spectrum the 9-H proton of IX appears as a singlet at 4.78 ppm and the signals for the protons of the pyridine ring are double doublets ($J_{1,2}$ = 7.5; $J_{1,3}$ = 1.5; $J_{2,3}$ = 5 Hz) at 8.32 and 8.50 (3-H); 6.68 and 6.95 (2-H); 6.40 and 7.24 ppm (1-H). The four protons of the phenyl ring appear as multiplets in the regions 8.0-8.15 and 7.3-7.8 ppm with relative integrated intensities of 1:3. In the PMR spectra of the halogen compounds III and V at room temperature all of the lines are broad ($\nu_{\frac{1}{2}} > 10$Hz), pointing to an increased rotational barrier of the azafluorenyl ring around the linking C—C bond upon exchange of hydrogen in compound IX for halogen atoms. The chemical shifts of 8.3-8.5 (3-H); 7.6-7.8 (5-H); 7.1-7.6 (1-H, 6-H to 8-H) and 6.8-7.1 (2-H) and the integrated intensities of 1:1:4:1 correspond to the expected values for protons of an azafluorene ring. At a temperature of 338°C the lines are narrowed to a sufficient extent to observe the characteristic spin-spin coupling of the pyridine ring in the azafluorene fragment.

EXPERIMENTAL

IR spectra were recorded on an IR-20 spectrophotometer as KBr tablets and PMR spectra on Tesla BC 467 (60 MHz) and Bruker AM-2590 spectrometers in $CDCl_3$ solvent with TMS as internal standard. The reactions wre monitored and the purities of the products assessed using TLC on Al_2O_3 activity II using ether: hexane (1:1) as eluent. Molecular weights were determined mass spectrometrically using an MK-1303 spectrometer with an ionizing energy of 70 eV.

Elemental analytical data for C, H, N, Hal (compounds II, III, and IV) and N (compound IX) agreed with those calculated.

9-Chloro-4-azafluorene (II, $C_{12}H_8ClN$). A. A solution of thionyl chloride (1.7 g, 14 mmole) in benzene (20 ml) was poured into a solution of azafluorenol I (9.55 g, 3 mmole) in benzene (20 ml) and held for 1 h at 20°C. Benzene and excess thionyl chloride were distilled off and water (15 ml) and a solution of sodium carbonate were added to pH 9. The product was extracted with ether (3 × 10 ml), dried with H_2CO_3, the ether distilled off, and the residue chromatographed on Al_2O_3 activity IV (h = 50 cm, d = 2 cm) with heptane heated to ~95°C as eluent. The product (0.5 g, 83%) was the chloride II and was a light-yellow crystalline material with mp 103-104.5°C (hexane) and Rf 0.8. PMR spectrum: 5.67 (1H, s, 9-H); 7.90 (1H, dd, 1-H); 7.21 (1H, dd, 2-H); 8.60 (1H, dd, 3-H); 7.9-8.1 (1H, m, 5-H); 7.3-7.8 ppm (3H, m, 3-H to 8-H). Found: M^+ 201, 203. Calculated: M 201.

B. A mixture of azafluorene I (0.3 g, 1.6 mmole) and thionyl chloride (1.0 g, 8.5 mmole) was held at 20°C for 1.5 h and worked up as above to give II (0.2 g, 76%).

Bis[9-chloro-4-azafluoren-9-yl] (III, $C_{24}H_{14}Cl_2N_2$). A. Azafluorene I (0.5 g, 2.7 mmole) and thionyl chloride (1.7 g, 14 mmole) were refluxed for 1 h, excess thionyl chloride distilled off, and the product worked up as described for II. It was extracted with chloroform (3 × 15 ml) and chromatographed to give II (0.42 g, 76.7%) as pale yellow crystals with mp 257.5-259°C (heptane) and Rf 0.5. Found: M^+ 400, 404. Calculated: M 400.

B. The chloride II (0.15 g, 0.7 mmole) and thionyl chloride (0.8 g, 6.7 mmole) were refluxed for 2 h. After similar treatment chromatography gave II (0.13 g, 87%) with mp 257-259°C.

Compound III was obtained in the same yield from alcohol I or chloride II with thionyl chloride in benzene.

Bis[9-bromo-4-azafluoren-9-yl] (V, $C_{24}H_{14}Br_2N_2$). A. The bromide IV (1.0 g, 4 mmole), thionyl chloride (5.0 g, 42 mmole), and benzene (30 ml) were refluxed for 3 h and worked up as described for II to give V (0.5 g, 50%) as dark yellow crystals with mp 244-245°C (decomp) (from a mixture of heptane and benzene) and Rf 0.3. Found: M^+ 488, 490, 492. Calculated: M 490.

A crystalline mixture (0.46 g) of 9,9-dichloro-4-azafluorene (VI) and 4-azafluoren-9-one (VII) was obtained as a crystalline solid, the composition of which was confirmed by comparison of the mass spectrum and the TLC with those of known samples.

B. Bromide IV (1.0 g, 4 mmole) and thionyl chloride (5.0 g, 42 mmole) were refluxed for 3 h. After a similar work-up chromatography gave V, VI, and VIII in succession. Elution with hexane gave the dichloride VI (0.52 g, 45%) with mp 139-140°C (heptane) [4]. A mixture of ether and hexane (3:1) gave V (0.2 g, 20%) with mp 245-246°C and, eventually with this solvent, compound VIII (0.1 g, 23%) with mp 288-289°C (from heptane) [5].

C. Bromine (1.0 g, 12.48 mmole) was added at 5-6°C to a solution of VIII (0.2 g, 0.6 mmole) in benzene (20 ml) and held for 3 h. After distillation of the benzene, water (20 ml) and a solution of sodium carbonate (20 ml) were added to pH 10. Extraction with chloroform (3 × 10 ml) and chromatography gave V (0.01 g, 8%).

Bis[4-azafluoren-9-yl] (IX, $C_{24}H_{16}N_2$). A. A solution of III (0.2 g, 0.5 mmole) in absolute ethanol (10 ml) was refluxed with activated zinc dust (0.5 g, 7.6 mmole) for 1 h. Alcohol was distilled off and water (10 ml) and sodium carbonate were added to pH 8. The product was extracted with chloroform (2 × 10 ml) and the extract dried with potassium carbonate. After distillation of chloroform it was crystallized from a mixture of heptane and benzene (13:1) to give IX (0.08 g, 50%) as colorless crystals with mp 283-284°C and Rf 0.6. Found: M^+ 332. Calculated: M 332.

B. V (0.08 g, 0.6 mmole), absolute alcohol (5 ml), and zinc dust (0.2 g, 3 mmole) were refluxed for 3 h to give IX (0.05 g, 93%) with mp 282-284°C.

Refluxing bromide IV with zinc dust in absolute ethanol gave 4-azafluorene (90%) with mp 93-94°C.

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TAUTOMERS OF AZINE DERIVATIVES.

21.* TAUTOMERISM IN 2-(2-HYDROXYARYL)AZINES

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Tautomerism in 2-(2-hyroxyaryl)azines has been studied using ^{17}O NMR and UV spectroscopy. Consideration has been given to the influence of solvent and structural factors which facilitate the establishment of a tautomeric equilibrium in these compounds.

A study of tautomerism in 2-hydroxyarylazines of the type A ⇆ B (Scheme 1) is of value for an understanding both of the properties of the azine fragment and of tautomerism in compounds of the phenol series. Work on this class of compound is also of practical value in so far as many 2-hydroxyarylazines possess light-stabilizing and complex-forming properties [2, 3].

The ability of 2-hydroxyarylazines to form tautomers with the participation of the ylidene form B has been much discussed in the literature [4-6]. The possibility of realizing the NH form had already been formulated by A. E. Chichibabin in 1918 [4] during a study of the simplest example of the 2-hydroxyarylazines – 2-(2-hydroxyphenyl)pyridine. In the 1970s, R. Abramovich [5, 6], on the basis of IR spectra in KBr, assigned to 2-(2-hydroxy-5-nitrophenyl)pyridine III the zwitterion structure IIIB' which, as can easily be seen, represents an NH type tautomer in the form of its other resonance hybrid. Nevertheless, there are at present no reliable data on tautomerism in 2-hydroxyarylazines in the literature.

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*Communication 20, see [1].

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