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BENZO[*f*]-3-AZA- AND -10-AZAFLUOROANTHENES

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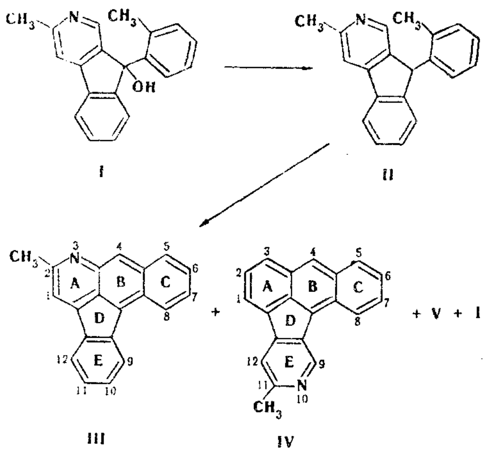
Reduction of 3-methyl-9-(o-tolyl)-2-azafluoren-9-ol (I) with tin in hydrochloric acid gave 3-methyl-9-(o-tolyl)-2-azafluorene, dehydrocyclization of which on a K-16 catalyst at 520-500°C gave a complex mixture, from which four substances – 2-methylbenzo[*f*]-3-azafluoranthene, 11-methylbenzo[*f*]-10-azafluoranthene, benzo[*f*]-3-azafluoroanthene (II), and I – were isolated and identified by means of the IR, UV, and PMR, and mass spectra. It is shown that the dehydrocyclization proceeds through the hydrogen atoms of the methyl group of the tolyl substituent and takes place at the 8-C or 1-C atom of the azafluorene system. The formation of products II and I constitutes evidence that the reaction is accompanied by partial demethylation or oxidation.

3-Methyl-9-(o-tolyl)-2-azafluoren-9-ol (I), which we described in [1], was used as the starting compound for the synthesis of benzo[*f*]-3-aza- and -10-azafluoranthene systems. Reduction of this alcohol with tin in hydrochloric acid gave 3-methyl-9-(o-tolyl)-2-azafluorene (II), which was subjected to dehydrocyclization in a K-16 catalyst at 520-550°C. Four crystalline compounds were isolated from the resulting complex mixture of substances by chromatography.



In all cases involving the formation of a benzoazafluoranthene structure (III-V) dehydrocyclization proceeds through the hydrogen atoms of the methyl group of the o-tolyl substituent of azafluorene II. Dehydrocyclization in the α position of the pyridine ring leads to the formation of 2-methylbenzo[*f*]-3-azafluoranthene

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(III), which we have previously obtained [2] by dehydrocyclization of 3,6-dimethyl-4-phenyl-2-benzylpyridine. 11-Methylbenzo[*f*]-10-azafluoranthene (IV) is formed as a result of cyclization in the 8-C position of azafluorene II. The UV spectra of III and IV contain bands in the longer-wave region as compared with the spectrum of starting II; this is due to the additional conjugation as a result of the formation of a condensed system. The UV spectra of these compounds are similar to the spectrum of 2,3-benzofluoranthene [3]. The presence of maximally intense molecular ion peaks in the mass spectra of III and IV and of intense peaks of doubly charged M^{++} ions (10%) confirms the condensed character of these substances. The formation of $[M-CH_3]^+$, $[M-HCN]^+$, and $[M-CH_3CN]^+$ fragments attests to the presence of a methyl group and a nitrogen atom in the molecules, with the methyl group in the α position of the pyridine ring.

The structures of benzoazafluoranthenes III and IV are confirmed also by the PMR spectral data. The spectrum of III does not contain a singlet signal of the α proton of the pyridine ring (8.5-9.5 ppm; 3a position). The singlet at 8.23 ppm is due to the proton attached to 4-C. The multiplet centered at 8.28 ppm belongs to the proton attached to 8-C. A three-proton singlet of the methyl group attached to 2-C (2.74 ppm) is present in the strong-field region. A singlet at 9.12 ppm due to the α proton of the pyridine ring is observed in the PMR spectrum of IV. The presence of this signal indicates that cyclization took place at 5-C. The broad weakly resolved doublet at 8.26 ppm (1H) belongs to 8-H. The singlet at 8.12 ppm (1H) is due to the proton attached to 4-C. The shift of the signal of the pyridine α proton to weak field as compared with the spectra of unsubstituted pyridine and 2-azafluorene and the considerable magnitude of the chemical shift of the proton attached to 8-C are probably due to the presence of stronger ring currents in the C and E rings than in the A and B rings [4]. The singlet at 2.56 ppm (3H) belongs to the protons of the methyl group attached to 11-C.

The formation of benzoazafluoranthenes from azafluorene II is accompanied by demethylation. This conclusion can be drawn on the basis of data from the PMR and mass spectra (presented in the experimental section) of the isolated fraction of crystals with mp 219-220°C, containing mainly (~70%) benzo[*f*]-3-azafluoranthene (V), which does not contain a methyl group.

The dehydrocyclization of azafluorene II is accompanied by its partial oxidation to azafluorenol I; this was proved by isolation of this alcohol [1] from the reaction products and subsequent identification.

An adduct with maleic anhydride was obtained from benzoazafluoranthene III. A bromide, to which the 4-bromo-2-methylbenzo[*f*]-3-azafluoranthene structure (VI) was assigned in analogy with the product formed in the bromination of anthracene, was isolated in the bromination of III. In the hydrogenation of III and IV in alcohol over platinum the amount of absorbed hydrogen corresponds to the hydrogen attached to the meso position of the three-ring ABC system; the initially brightly colored solution becomes colorless. However, we were unable to isolate the hydrogenation products. On contact with air the solution rapidly takes on its initial color, and the reaction products contain the starting compound.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were measured with a UR-20 spectrometer. The UV spectra of ethanol solutions were recorded with a Hitachi EPS-3 recording spectrophotometer. The PMR spectra of $CDCl_3$ solutions were obtained with Varian HA-100D and Tesla BS-487C spectrometers with tetramethylsilane as the internal standard. The mass spectra were measured with an MKh-1303 mass spectrometer. Chromatography with a column filled with activity II aluminum oxide and in a thin layer of the same adsorbent was accomplished by elution with ether–hexane (1 : 3) in the first case and with ether in the second case.

3-Methyl-9-(o-tolyl)-2-azafluorene (II). An 8-g (0.013 g-atom) sample of tin was added to a solution of 2 g (7 mmole) of azafluorenol I in 30 ml of ethanol and 15 ml of 36% hydrochloric acid, and the mixture was heated until the reaction commenced. At the end of the spontaneous reaction, the mixture was heated at 80°C for 1 h. The alcohol and acid were removed by distillation, the residue was diluted with water, the mixture was saturated with sodium carbonate, and the reaction products were extracted with ether. The ether extract was dried with sodium sulfate and worked up to give 1.5 g (80.8%) of azafluorene II with mp 107-108°C (from ligroin) and R_f 0.82. IR spectrum: 3074 and 3025 cm^{-1} (aromatic C–H) and 1616 cm^{-1} (aromatic ring C=C). Found: C 88.2; H 6.1; N 4.9%. $C_{20}H_{17}N$. Calculated: C 88.5; H 6.2; N 5.1%.

Dehydrocyclization of 3-Methyl-9-(o-tolyl)-2-azafluorene. The reaction was carried out in a flow system with a quartz contact tube and packing and 15 ml of K-16 catalyst. A solution of 5 g (0.018 mole) of azafluorene II in 20 ml of benzene was passed at a contact rate for 2.5 h through the contact tube at 520-550°C. A total of 0.85 liter of gas was collected (23°C, 770 mm; H_2 92%, C_nH_{2n} 7%). The residue (2.54 g) remaining after removal of the benzene from the catalysate by distillation was separated with a chromatographic column (h =

62 cm), d = 2.5 cm). The following crystal fractions were isolated successively. 1) A total of 0.73 g (2.7 mmole) of starting azafluorene II with mp 106-108°C and R_f 0.82. 2) A total of 0.13 g (3%) of bright-yellow crystals of 2-methylbenzo[*f*]-3-azafluoranthene (III) with mp 188-189°C (from hexane) and R_f 0.63. Found: C 89.6; H 5.4; N 5.0%; M 267 (mass spectrometrically). $C_{20}H_{13}N$. Calculated: C 89.9; H 4.9; N 5.2%; M 267. 3) A total of 0.1 g (2.3%) of orange crystals of 11-methylbenzo[*f*]-10-azafluoranthene (IV) with mp 197-198°C (from hexane) and R_f 0.45. Found: C 89.8; H 5.6; N 5.1%; M 267 (mass spectrometrically). $C_{20}H_{13}N$. C 89.9; H 4.9; N 5.2%; M 2.67. The hydrochloride had mp 212-214°C (from alcohol). Found: Cl 11.4; N 4.8%. $C_{20}H_{13}N \cdot HCl$. Calculated: Cl 11.7; N 4.6%. 4) A mixture of ~ 70% benzo[f]-3-azafluoranthene (V) and ~ 30% 3-methyl-9-(o-tolyl)-2-azafluoren-9-ol (I) (a total of 0.1 g) with mp 219-220°C (from hexane). The maximally intense ion peak in the mass spectrum with m/e 253 corresponds to the molecular weight of V; the $[M-CH_3]^+$ ion peak is absent. The PMR spectrum does not contain the signal of a methyl group that is characteristic for substituted benzo[*f*]-3-azafluoranthene III. The doublet at 8.89 ppm (1H, J = 5 Hz) is related to the proton attached to 11-C. Data from the PMR and mass spectra of the product isolated from the mixture attest to the presence in this fraction of alcohol I: the mass spectrum contains a molecular ion peak with m/e 287 and a maximally intense peak with m/e 196 (100%) belonging to the $[M-C_6H_5CH_3]^+$ ion; the PMR spectrum contains peaks at δ 2.37 (CH_3 attached to 3-C), 1.24 (CH_3 group of the tolyl substituent), and 7.60 ppm (OH). Also obtained was 0.1 g of 3-methyl-9-(o-tolyl)-2-azafluoren-9-ol (I) with mp 224-225°C (from hexane) and R_f 0.12 [1].

Reaction of 0.1 g (0.37 mmole) of III and 0.15 g (1.53 mmole) of maleic anhydride by refluxing from 6 h in benzene gave 0.09 g (66%) of an adduct as dark-brown crystals with mp 250°C (dec.) that were insoluble in any solvents. Found: N 3.7%. $C_{24}H_{15}NO_3$. Calculated: N 3.8%.

Treatment of 0.1 g (0.37 mmole) of III with 0.06 g (0.37 mg-atom) of bromine in carbon tetrachloride yielded 0.07 g (54%) of red crystals of VI with mp 250°C (dec.). Found: Br 23.2; N 3.7%. $C_{20}H_{12}BrN$. Calculated: Br 23.1; N 4.0%.

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