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HYDROGENATION AND HALOGENATION OF 6-PHENYL-5-AZABENZO[f]FLUORANTHENE AND REDUCTION OF ITS ADDUCTS WITH ACRYLONITRILE

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The hydrogenation of 6-phenyl-5-azabenzo[f]fluoranthene in the presence of rhenium heptasulfide takes place in the meso positions of its azaanthracene fragment. The reaction of 5-azabenzo[f]fluoranthene with acid chlorides and aluminum chloride in nitrobenzene gives its 8-chloro derivative. The reduction of the adducts of the diene synthesis of 6-phenyl-5-azabenzo[f]fluoranthene with acrylonitrile by means of sodium in butyl alcohol leads to the corresponding aminomethyl derivatives and a product of retrodiene synthesis, viz., the starting azabenzofluoranthene. The reduction of the adduct of the diene synthesis of 1,3-diphenyl-2-azaanthracene with acrylonitrile proceeds similarly.

6-Phenyl-5-azabenzo[f]fluoranthene (I), which was obtained by catalytic dehydrocyclization of 3-methyl-4-benzyl-2,6-diphenylpyridine [1], is a relatively complex heterocyclic compound with several reaction centers that are structurally similar to certain alkaloids [2]. Considering the rather practicable method for its synthesis, we undertook a study of some of its chemical transformations.

The hydrogenation of azabenzofluoranthene I in the presence of rhenium heptasulfide takes place in the meso positions of its azaanthracene fragment; only one substance, viz., 6-phenyl-8,12b-dihydro-5-azabenzo[f]fluoranthene (II), which was isolated in the form of the hydrochloride, is formed in quantitative yield. The free base of dihydro derivative II is a more labile compound than its nitrogen-free analog 8,12b-dihydrobenzo[*a*]fluoranthene [3]. When II is stored or when it is refluxed briefly in solution in benzene or passed through a layer of Al_2O_3, it is dehydrogenated to give starting azabenzofluoranthene I.

When I is subjected to reaction with acetyl chloride or with benzoyl chloride in nitrobenzene in the presence of a 10-15-fold excess of aluminum chloride, it undergoes chlorination. 8-Chloro-6-phenyl-5-azabenzo[f]fluoranthene (III) was synthesized in greater than 70% yield by this method. The same chloro derivative was obtained in 13% yield by refluxing azabenzofluoranthene I with aluminum chloride in nitrobenzene. The reaction of azabenzofluoranthene I with acid chlorides evidently gives complexes of its $C_{(8)}$ acyl derivatives with aluminum chloride, the subsequent decomposition of which leads to the chloro derivative. 8-Bromo-6-phenyl-5-azabenzo[f]fluoranthene (IV) was isolated in low yield in the bromination of I with cupric bromide in nitrobenzene.

The diene condensation of azabenzofluoranthene I with acrylonitrile, in which a mixture of isomeric (with respect to the position of the cyano group in the ethylene bridge) adducts,

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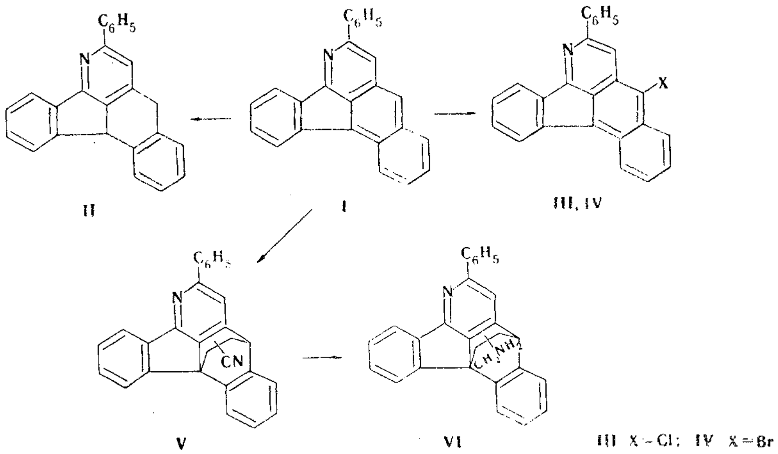
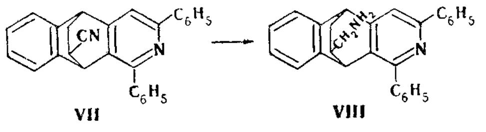


viz., 8H-6-phenyl-8,12b-(2-cyanoethylene)[1-cyanoethylene]-5-azabenzo[f]fluoranthenes (V), is formed, has been described [4]. In order to obtain amino derivatives of these heterocycles we carried out the reduction of a mixture of V by the Bouveault–Blanc method; retrodiene fragmentation occurs along with reduction in this case. Starting nitrile V, azabenzofluoranthene I, and 8H-6-phenyl-8,12b-(aminomethylethylene)-5-azabenzo[f]fluoranthene (VI) (the position of the aminomethyl group has not yet been established) were isolated from the reaction mixture by chromatography.

We used this method to reduce the previously described [4] 9,10-dihydro-1,3-diphenyl-9,10-(1-cyanoethylene)-2-azaanthracene (VII).



Retrodiene fragmentation to give 1,3-diphenyl-2-azaanthracene also occurs in this case. 9,10-Dihydro-1,3-diphenyl-9,10-(1-aminoethylene)-2-azaanthracene (VIII) was obtained in 25% yield.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra of solutions of the compounds in alcohol were recorded with a Specord UV-vis spectrophotometer. The PMR spectrum was recorded with a Hitachi–Perkin-Elmer spectrometer with tetramethylsilane as the internal standard. The mass spectra were recorded with an MKh-1303 spectrometer. Chromatography with a column and in thin layers was realized on Brockman activity II Al_2O_3 in an ethyl acetate–heptane system (1:4).

6-Phenyl-8,12b-dihydro-5-azabenzo[f]fluoranthene (II). A 0.5-g (1.52 mmole) sample of azabenzofluoranthene I was hydrogenated at 240°C in the course of 5 h in 15 ml of benzene in the presence of 0.03 g of rhenium heptasulfide. The initial hydrogen pressure was 210 atm. The catalyst was removed by filtration. According to thin-layer chromatography (TLC), the hydrogenation proceeded quantitatively, and a substance with R_f 0.62 was formed. The filtrate was divided into three parts, which were worked up as indicated below.

a) Hydrogen chloride was passed into the first part. The precipitate (0.15 g) was crystallized from acetone to give 0.09 g of the hydrochloride of II as colorless crystals with mp 115-116°C and R_f 0.62. UV spectrum, λ_{max} (log ε): 205 (4.70), 214 (4.70), 235 (4.83), 242 (4.60), 304 (4.10), 316 (4.28), 332 (4.14), 338 nm (4.14). PMR spectrum (in $CDCl_3$): 3.60 (1H, s, 12b-H) and 2.90 ppm (2H, s, CH_2). Found: C 81.8; H 5.2; Cl 9.9; N 4.1%. $C_{25}H_{18}N \cdot HCl$. Calculated: C 81.6; H 5.1; Cl 9.7; N 3.8%.

b) The residue (0.16 g) remaining after removal of the benzene from the second part by distillation at atmospheric pressure was crystallized from heptane to give 0.12 g of starting azabenzofluoranthene I as orange crystals with mp 154-155°C. No melting-point depression was observed for a mixture of this product with a standard sample.

c) The third part was passed through a column (h = 25 cm, d = 2.5 cm, heptane). Workup gave 0.2 g of azabenzofluoranthene I with mp 154-155°C and R_f 0.56.

8-Chloro-6-phenyl-5-azabenzo[f]fluoranthene (III). A) A solution of 3 g (22 mmole) of aluminum chloride in 15 ml of nitrobenzene was added at 0°C to a solution of 1.02 g (14 mmole) of acetyl chloride and 1 g (3.04 mmole) of azabenzofluoranthene I in 50 ml of nitrobenzene, and the mixture was maintained at 0°C for 1 h. It was then heated at 190-200°C for 5 h, after which it was decomposed with 100 ml of water. The organic bases were extracted with ether, the extract was dried with magnesium sulfate, the ether and nitrobenzene were removed by distillation, and the residue (0.95 g) was chromatographed with a column (h = 30 cm, d = 2.5 cm, heptane) to give 0.85 g (77%) of III as red crystals with mp 218-219°C [from heptane—ethyl acetate (2:1)] and R_f 0.72. UV spectrum, λ_{max} (log ε): 204 (4.20), 218 (4.18), 250 (4.02), 282 (4.40), 348 (3.28), 367 (3.00), 456 (3.38), 480 nm (3.36). Found: C 82.5; H 4.0; Cl 9.6; N 3.7%; M^+ 363. $C_{25}H_{14}ClN$. Calculated: C 82.6; H 3.9; Cl 9.6; N 3.9%; M 363.

B) A similar method gave 0.39 g (70%) of chloro-substituted azabenzofluoranthene III, with mp 218-219°C [heptane—ethyl acetate (2:1)] and R_f 0.72, from 0.5 g (1.5 mmole) of azabenzofluoranthene I and 1 g (7 mmole) of benzoyl chloride in 60 ml of nitrobenzene in the presence of 2 g (14.7 mmole) of aluminum chloride. No melting-point depression was observed for a mixture of this product with a sample obtained in experiment A.

C) A solution of 0.2 g (0.6 mmole) of azabenzofluoranthene I and 0.8 g (6 mmole) of aluminum chloride in 35 ml of nitrobenzene was heated at 190-210°C for 6 h, after which it was decomposed with 50 ml of water. The reaction products were extracted with ether, and the extract was dried with magnesium sulfate. The ether and nitrobenzene were removed from the extract by distillation, and the residue was chromatographed with a column (h = 10 cm, d = 1.5 cm, heptane) to give successively 0.04 g (13%) of III with mp 218-219°C [heptane—ethyl acetate (2:1)] and 0.16 g of starting azabenzofluoranthene I.

8-Bromo-6-phenyl-5-azabenzo[f]fluoranthene (IV). A mixture of 0.2 g (0.6 mmole) of azabenzofluoranthene I, 0.24 g (1.8 mmole) of anhydrous cupric bromide, and 25 ml of nitrobenzene was heated at 160-170°C for 4 h, after which the nitrobenzene was removed by distillation, and the residue was chromatographed with a column (h = 20 cm, d = 2.5 cm, petroleum ether) to give initially 0.005 g of bromide IV as red crystals. Found: M^+ 408. $C_{25}H_{14}BrN$. Calculated: M 408. Subsequent elution gave 0.15 g of starting azabenzofluoranthene I.

8H-6-Phenyl-8,12b-(aminomethylethylene)-1-azabenzo[f]fluoranthene (VI). A 1-g (0.044 mole) sample of sodium was added gradually to a refluxing solution of 1 g (2.6 mmole) of a mixture of nitriles V in 50 ml of n-butanol, and the mixture was refluxed for 2 h. Water (100 ml) was then added, and the solution of reaction products in the butanol was separated. The aqueous layer was extracted with butanol (two 25-ml portions), the butanol was removed by distillation, and the residue (0.87 g) was chromatographed with a column (h = 20 cm, d = 2 cm). Elution with heptane gave 0.15 g (17.4%) of azabenzofluoranthene I (mp 154-155°C), subsequent elution with heptane—ethyl acetate (10:1) gave 0.16 g (15.6%) of a mixture of nitriles V, and elution with ethanol gave 0.48 g (48%) of VI with mp 212-213°C. UV spectrum, λ_{max} (log ε): 208 (4.94), 241 (4.74), 276 (4.22), 294 (4.12), 324 nm (4.38). IR spectrum: 3368 (ν_{NH_2}) and 1685 cm^{-1} (δNH). Found: C 87.1; H 5.6; N 6.9%; M^+ 386. $C_{28}H_{22}N_2$. Calculated: C 87.0; H 5.7; N 7.2%; M 386.

9,10-Dihydro-1,3-diphenyl-9,10-(1-aminomethylethylene)-2-azaanthracene (VIII). The reaction of 1 g (2.6 mmole) of VII, 100 ml of n-butanol, and 1 g (0.04 mole) of sodium metal was carried out similarly. The reaction products (0.85 g) were chromatographed. Elution with petroleum ether gave 0.11 g (13%) of 1,3-diphenyl-2-azaanthracene, subsequent elution with heptane—ethyl acetate (10:1) gave 0.35 g (35%) of starting nitrile VII, and elution with ethanol gave 0.25 g (25%) of amino derivative VIII with mp 133-134°C. IR spectrum: 3440 (ν_{NH_2}) and 1670 cm^{-1} (δNH). Found: N 7.3%; M^+ 388. $C_{28}H_{24}N_2$. Calculated: N 7.2%; M 388.

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