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Heterocyclic Analogs of Pleiadiene: LXXIV.* *peri*-Cyclizations in the Perimidine Series. Synthesis of 1,3-Diazapyrene Derivatives

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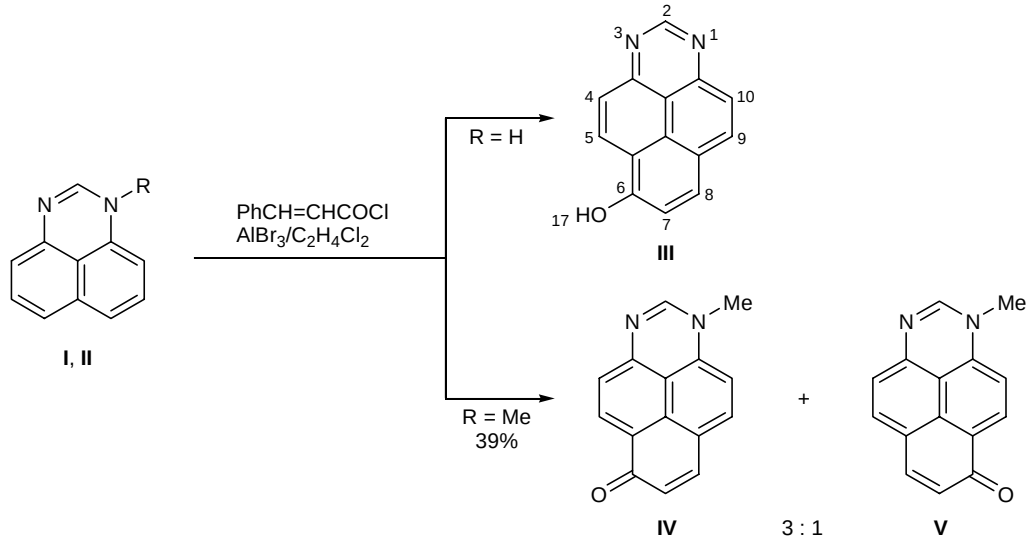
Abstract—Reactions of perimidines and perimidin-2-ones with α,β-unsaturated carbonyl compounds gave various 1,3-diazapyrene derivatives. Acylation of 1-methylperimidine, perimidin-2-one, and 1-methylperimidin-2-one with cinnamoyl chloride in the presence of $AlBr_3$ is accompanied by *peri*-fusion at the 6,7-position and dearylation of the intermediate product. Under analogous conditions, 1,3-dimethyl-2,3-dihydroperimidine gave rise to 6-cinnamoyl-1,3-dimethyl-2,3-dihydroperimidine. Reactions of perimidin-2-ones with 1,3-diphenyl-2-propenone in polyphosphoric acid resulted in *peri*-fusion at the 6,7-position, and with acetylacetone, at the 1,9-position.

We previously developed several one-step procedures for 6,7-*peri*-fusion to perimidines, which allowed us to synthesize various derivatives of poorly studied 1,3-diazapyrene [2–6]. In particular, the acylation of perimidine (**I**) with cinnamoyl and *p*-bromocinnamoyl chlorides in the presence of excess $AlBr_3$ occurred at the 6(7)-position and was accompanied by intramolecular cyclization at the adjacent *peri*-position and dearylation to afford 1,3-diazapyren-6-ol (**III**) in both cases [4, 6] (Scheme 1).

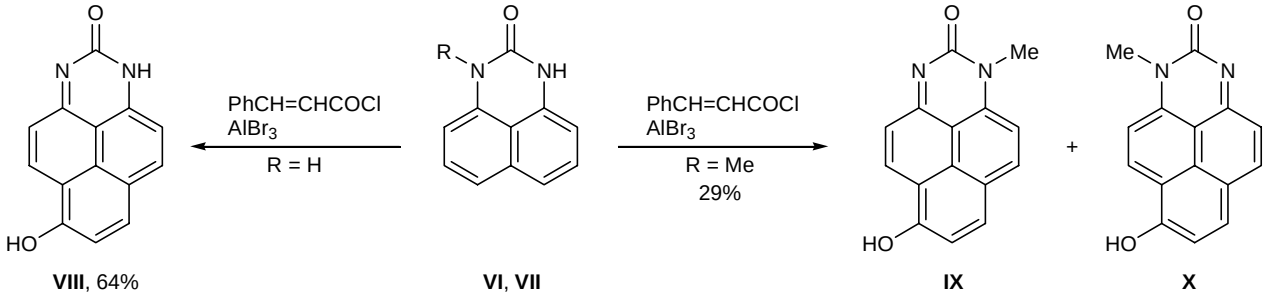
Scheme 1.



I, R = H; **II**, R = Me.

* For communication LXXIII, see [1].

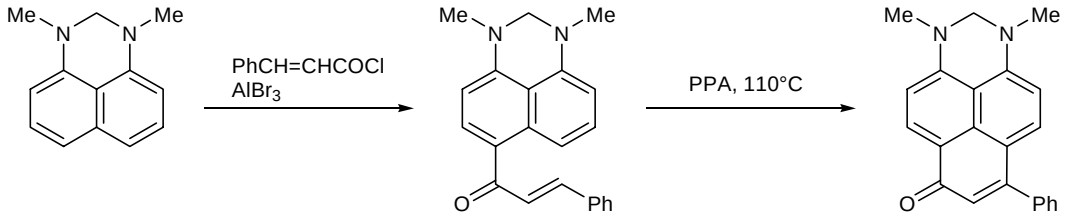
Scheme 2.



VIII, 64% **VI**, **VII** **IX** **X**

VI, R = H; **VII**, R = Me.

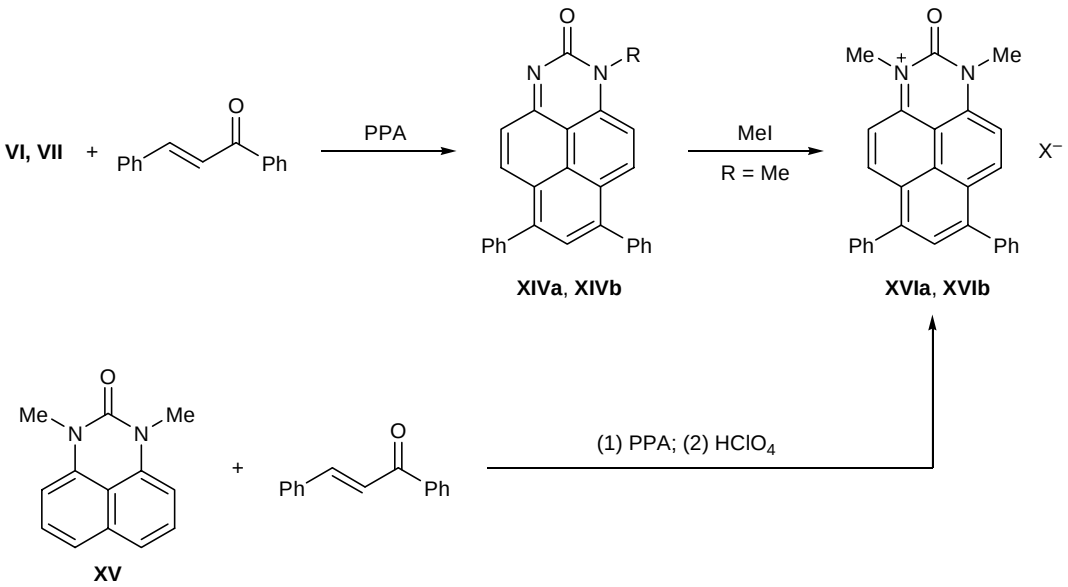
Scheme 3.



XI **XII** **XIII**

The goal of the present work was to examine the above and other *peri*-cyclizations in the series of 1-substituted perimidines, perimidin-2-ones, and 2,3-dihydroperimidines. 1-Methylperimidine (**II**) reacted with cinnamoyl chloride in the presence of $AlBr_3$ even at room temperature, yielding a mixture of isomeric 1-methyl-1,6-dihydro-1,3-diazapyren-6-one (**IV**) and 1-methyl-1,8-dihydro-1,3-diazapyren-8-one (**V**) (see Scheme 1); we failed to separate this mixture. According to the ^1H NMR data, isomer **IV** was the major product. Analogous tandem reactions were observed for 2,3-dihydro-1*H*-perimidin-2-one (**VI**) and 1-methylperimidin-2(1*H*)-one (**VII**). In the first case, 6(8)-hydroxy-1,2-dihydro-1,3-diazapyren-2-one (**VIII**)

Scheme 4.



XIVa, **XIVb** **XVIa**, **XVIb** **XV**

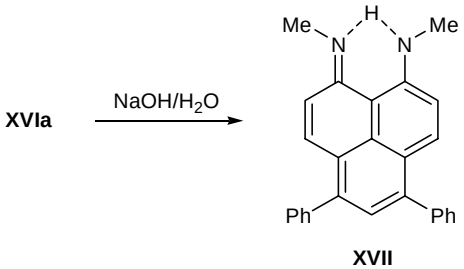
XIV, R = H (**a**), Me (**b**); **XVI**, X = ClO_4 (**a**), I (**b**).

was formed, and in the second, a mixture of isomeric 6- and 8-hydroxy-1-methyl-1,2-dihydro-1,3-diazapyren-2-ones **IX** and **X** at a ratio of 9:1 (according to the ^{1}H NMR data; Scheme 2). However, the reaction of 1,3-dimethyl-2,3-dihydro-1*H*-perimidine (**XI**) with cinnamoyl chloride in the presence of $AlBr_3$ stops at the stage of formation of 6-cinnamoyl-1,3-dimethyl-2,3-dihydro-1*H*-perimidine (**XII**) (Scheme 3). A probable reason is formation of a stable complex with $AlBr_3$ at the nitrogen atom, which hampers subsequent intramolecular alkylation of compound **XII**. The latter underwent cyclization only at 110°C in polyphosphoric acid (PPA), i.e., under the conditions corresponding to the formation of ketone **XIII** from compound **XI** and cinnamic acid [7].

Like perimidine [3], reactions of perimidin-2-ones **VI** and **VII** with 1,3-diphenyl-2-propenone (chalcone) in PPA resulted in 6,7-*peri*-cyclizations with formation of 6,8-diphenyl-1,2-dihydro-1,3-diazapyren-2-one (**XIVa**) and its *N*-methyl derivative **XIVb**, respectively. The reaction of 1,3-dimethylperimidin-2-one (**XV**) with chalcone was accompanied by aromatization, leading to 1,3-dimethyl-6,8-diphenyl-2-oxo-2,3-dihydro-1,3-diazapyrenium cation which was isolated as perchlorate **XVIa** (Scheme 4). The latter was also obtained by quaternization of **XIVb** with methyl iodide, followed by exchange of iodide ion for ClO_4^-. Unlike yellow–green perchlorate, iodide **XVIb** is dark violet, presumably due to formation of an autocomplex between the cation of **XVI** and iodide ion in crystal. Such complexes are known to be formed from other heteroaromatic cations [8].

On heating with aqueous alkali, salt **XVIa** undergoes hydrolysis to give *N*,*N*'-dimethyl-9-amino-4,6-diphenyl-1*H*-phenalen-1-imine (**XVII**) (for structural analogs, see [9, 10]; Scheme 5). Compounds **XIVa** and **XIVb** did not change under similar conditions.

Scheme 5.

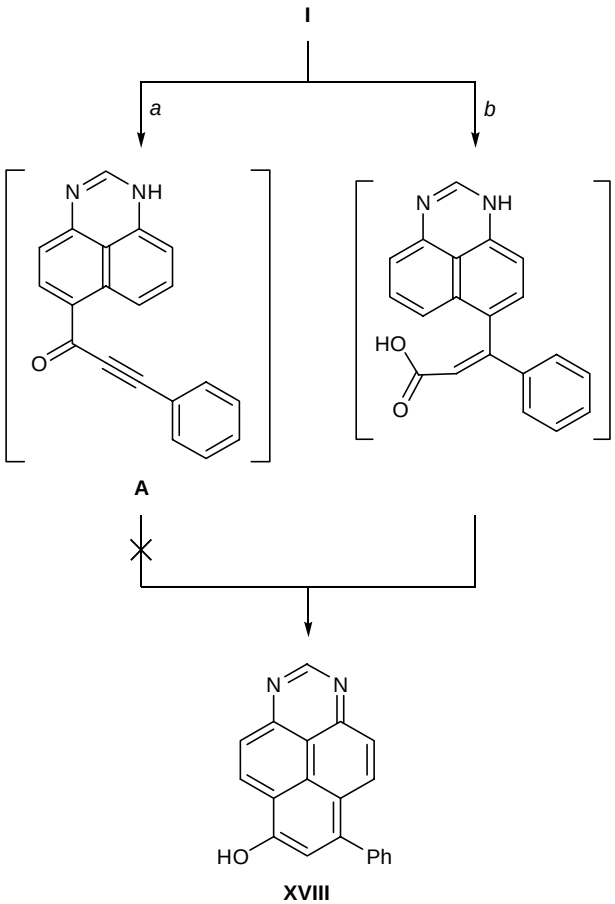


XVII

The reaction of 1,3-dimethyl-2,3-dihydro-1*H*-perimidine (**XI**) with chalcone in polyphosphoric acid resulted in formation of a complex mixture of unstable products.

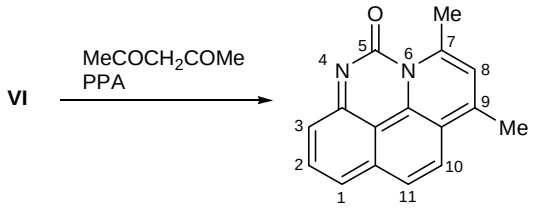
Such difunctional 1,3-electrophiles as β-keto acids, β-diketones, and acetylenic acids also seemed to be promising reagents for 6,7-*peri*-fusion of perimidine. However, in contrast to 1,3-dialkyl derivatives of perimidin-2-one, perimidine-2-thione, and 2,3-dihydroperimidine [7], perimidine (**I**) failed to react with ethyl acetoacetate in PPA at 70–80°C, while at higher temperature decomposition occurred. Compound **I** reacted with aceylacetone in polyphosphoric acid only above 100°C to give 4(9)-acetylperimidine in a poor yield [3]. The reaction of **I** with 3-phenylpropynoic acid in PPA at 120°C gave previously described 8-phenyl-1,3-diazapyren-6-ol (**XVIII**) [6]. Presumably, as in the reactions with cinnamic acid [6, 11], the process involves alkylation of perimidine (**I**) with ambident phenylpropynoyl cation (pathway *b* in Scheme 6). Alternative pathway *a* seems to be improbable because of unfavorable geometric structure of intermediate **A**.

Scheme 6.



XVIII

Scheme 7.



XIX, 87%

Unexpected results were obtained in the reaction of perimidin-2-one (**VI**) with acetylacetone in PPA. This reaction afforded 7,9-dimethyl-5*H*-pyrido[1,2,3-*cd*]-perimidin-5-one (**XIX**) via 1,9-*peri*-fusion (Scheme 7). Compound **XIX** is readily soluble in dilute mineral acids, and it forms yellow–green perchlorate which is insoluble in water. The latter is unstable: it decomposes on attempted recrystallization from alcohol. Neutral base **XIX** is also fairly unstable. It undergoes gradual tarring on storage, and heating of **XIX** in aqueous alkali for a short time or stirring in alcoholic alkali at room temperature leads to formation of 10-amino-2,4-dimethylbenzo[*h*]quinolin-10-amine (**XX**) or its *N*-ethoxycarbonyl derivative **XXI**, respectively, in a low yield (both reactions are accompanied by strong tarring; Scheme 8). 1,3-Dimethyl-2,3-dihydro-1*H*-perimidin-2-one (**XV**) also readily reacted with acetylacetone in PPA, but the product was a green crystalline oligomer.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker WP-200 spectrometer with TMS as internal reference; the signals were assigned using the double resonance technique. The mass spectra were obtained on an MKh-1321A instrument. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates.

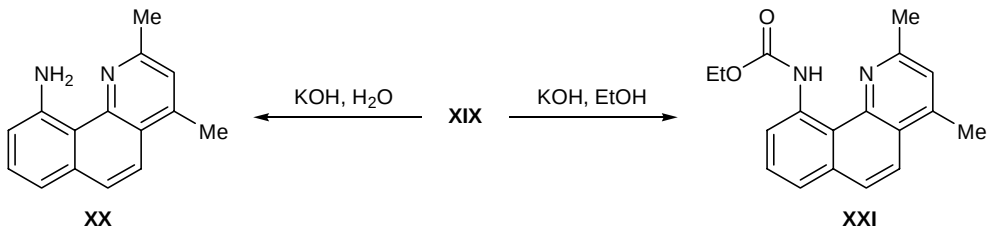
1-Methyl-1,6-dihydro-1,3-diazapyren-6-one (IV) and 1-methyl-1,8-dihydro-1,3-diazapyren-8-one (V). A solution of 0.216 g (1.3 mmol) of cinnamoyl chloride in 1 ml of dichloroethane was added dropwise under stirring to a mixture of 6 ml of dichloroethane, 2.67 g (10 mmol) of $AlBr_3$, and 0.18 g (1 mmol) of 1-methylperimidine, maintaining the temperature below 30°C. When the addition was complete, the mixture was stirred for 30 min at room temperature, carefully poured into 10 ml of water, and cooled, and 10 ml of petroleum ether was added. The precipitate was filtered off, dried, ground with 0.5 g of silica gel, and transferred to a chromatographic column charged with a small amount of silica gel (d = 2 cm, h = 1.5 cm). The column was eluted with methanol to obtain a yellow fraction. Removal of the solvent gave 0.15 g of a mixture of compounds **IV** and **V** as red–brown crystals (yield 39%).

Compound **IV**. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.83 d (1H, 10-H), 7.16 d (1H, 4-H), 7.52 d (1H, 8-H), 8.09 d (1H, 9-H), 8.23 d (1H, 5-H), 8.65 d (1H, 7-H); $J_{9,10}$ = 9.5, $J_{4,5}$ = 8.2, $J_{7,8}$ = 8.5 Hz; 8.60 s (1H, 2-H).

Compound **V**. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.83 d (1H, 10-H), 7.34 d (1H, 6-H), 7.39 d (1H, 4-H), 8.12 d (1H, 9-H), 8.22 d (1H, 5-H), 8.67 d (1H, 7-H); $J_{9,10}$ = 9.5, $J_{6,7}$ = 8.2, $J_{4,5}$ = 8.2 Hz; 8.56 s (1H, 2-H).

6(8)-Hydroxy-1,2-dihydro-1,3-diazapyren-2-one (VIII). Aluminum bromide, 2.67 g (10 mmol), was added to 5 ml of dichloroethane, the mixture was cooled to room temperature, and 0.184 g (1 mmol) of perimidinone **VI** and 0.216 g (1.3 mmol) of cinnamoyl chloride were added in succession. The reaction was complete in 1 h. The mixture was carefully poured into 15 ml of water, the remaining dichloroethane was distiled off, and the precipitate was filtered off and treated with several portions of boiling isopropyl alcohol. The solvent was distilled off to obtain 0.15 g (64%) of compound **VIII** as red–brown crystals with mp 298–300°C (decomp., from isopropyl alcohol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.47 d (1H, 7-H), 6.71 d (1H, 10-H), 6.86 d (1H, 4-H), 7.67 d (1H, 8-H), 7.78 d (1H, 9-H), 8.32 d (1H, 5-H); $J_{7,8}$ = 9.2,

Scheme 8.



XX **XXI**

$J_{9,10}$ = 8.2, $J_{4,5}$ = 8.7 Hz. Found, %: C 71.32; H 3.36; N 11.72. $C_{14}H_8N_2O_2$. Calculated, %: C 71.18; H 3.41; N 11.86.

6-Hydroxy-1-methyl-1,2-dihydro-1,3-diazapyren-2-one (IX) and 8-hydroxy-1-methyl-1,2-dihydro-1,3-diazapyren-2-one (X). Aluminum bromide, 2.67 g (10 mmol), was added to 5 ml of dichloroethane, the mixture was cooled to room temperature, and 0.198 g (1 mmol) of 1-methylperimidinone **VII** and 0.216 g (1.3 mmol) of cinnamoyl chloride were added in succession. The reaction was complete in 1 h. The mixture was carefully poured into 15 ml of water, the remaining dichloroethane was distilled off, and the precipitate was filtered off and treated with several portions of boiling isopropyl alcohol. The extract was evaporated to dryness to obtain 0.09 g (29%) of a mixture of compounds **IX** and **X** at a ratio of 9:1 (according to the ^{1}H NMR data); red–brown crystals.

Compound **IX**. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.56 d (1H, 7-H), 6.86 d (1H, 4-H), 6.88 d (1H, 10-H), 7.74 d (1H, 8-H), 7.92 d (1H, 9-H), 8.31 d (1H, 5-H); $J_{7,8}$ = 8.5, $J_{4,5}$ = 8.9, $J_{9,10}$ = 8.2 Hz.

Compound **X**. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.46 d (1H, 7-H), 6.73 d (1H, 4-H), 7.13 d (1H, 10-H), 7.74 d (1H, 8-H), 7.79 d (1H, 5-H), 8.53 d (1H, 9-H); $J_{7,8}$ = 8.1, $J_{4,5}$ = 8.2, $J_{9,10}$ = 8.5 Hz.

6-Cinnamoyl-1,3-dimethyl-2,3-dihydro-1*H*-perimidine (XII). Aluminum bromide, 2.67 g (10 mmol), was added to 5 ml of dichloroethane, the mixture was cooled to room temperature, and 0.197 g (1 mmol) of 1,3-dimethyl-2,3-dihydro-1*H*-perimidine and 0.216 g (1.3 mmol) of cinnamoyl chloride were added in succession. The reaction was complete in 30 min. The mixture was carefully poured into 15 ml of water and extracted with benzene (50 ml). The extract was washed with 10% aqueous ammonia, concentrated to a volume of 3 ml, and applied to a column charged with aluminum oxide. The column was eluted with benzene to isolate a yellow fraction. Removal of the solvent from the eluate gave 0.12 g (37%) of compound **XII** as orange–red crystals, mp 78–80°C (from octane). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.94 s and 3.07 s (3H each, NMe), 4.31 s (2H, CH_2), 6.55 d (1H, 4-H, $J_{4,5}$ = 8.2 Hz), 6.62 d (1H, 9-H, $J_{8,9}$ = 7.9 Hz), 7.4 m (5H, C_6H_5), 7.41 d.d (1H, 7-H, $J_{6,7}$ = 8.5, $J_{7,8}$ = 7.9 Hz), 7.57 d (1H, =CH–, J_{trans} = 15.6 Hz), 7.69 d (1H, =CHCO, J_{trans} = 15.6 Hz), 8.11 d (1H, 5-H, $J_{4,5}$ = 8.2 Hz), 8.26 d (1H, 6-H, $J_{6,7}$ = 8.5 Hz). Found, %: C 79.86; H 6.93; N 8.46. $C_{22}H_{22}N_2O$. Calculated, %: C 79.97; H 6.71; N 8.48.

1,3-Dimethyl-8-phenyl-1,2,3,6,7,8-hexahydro-1,3-diazapyren-6-one (XIII). A solution of 0.33 g (1 mmol) of 1,3-dimethyl-6-cinnamoyl-2,3-dihydro-1*H*-perimidine (**XII**) in 5 g of polyphosphoric acid was stirred for 1.5 h at 110°C. The mixture was cooled to 85°C, poured under vigorous stirring into ~30 ml of cold water, and neutralized with aqueous ammonia (pH ≈ 8). The precipitate was filtered off, washed with water, and dried. The product was treated with 3 ml of ethyl acetate, and the solution and the undissolved material were applied to a column charged with Al_2O_3. The column was eluted with benzene to isolate a yellow fraction. Removal of the solvent from the latter gave an oily substance which crystallized on grinding with diethyl ether. Yield 0.23 g (69%). Yellow crystals, mp 143–144°C (from benzene–petroleum ether) (cf. [7]).

6,8-Diphenyl-1,2-dihydro-1,3-diazapyren-2-one (XIVa). A mixture of 0.74 g (4 mmol) of perimidinone **VI**, 1.66 g (8 mmol) of 1,3-diphenyl-2-propenone, and 7 g of polyphosphoric acid was stirred for 6 h at 65–70°C. The mixture was poured into water and neutralized with aqueous ammonia to pH ≈ 8, and the precipitate was filtered off, washed with water, dried, and dissolved in 30 ml of ethanol on heating. The solution was heated at the boiling point with addition of charcoal, evaporated by half, and poured while hot into 50 ml of water. After 2 h, the precipitate was filtered off, washed with ethyl acetate, and dried. Yield 0.3 g (20%). Yellow crystals, mp 246–248°C (from ethanol–ethyl acetate). ^{1}H NMR spectrum (DMSO-d_6–CCl_4), δ, ppm: 7.40–7.65 m (12H, 4-H, 10-H, $2C_6H_5$), 7.76 s (1H, 7-H), 8.33 d (2H, 5-H, 9-H, $J_{4,5}$ = 9.4, $J_{9,10}$ = 9.4 Hz), 12.52 br.s (1H, NH). Found, %: C 83.68; H 4.55; N 7.29. $C_{26}H_{16}N_2O$. Calculated, %: C 83.85; H 4.33; N 7.52.

1-Methyl-6,8-diphenyl-1,2-dihydro-1,3-diazapyren-2-one (XIVb). A mixture of 0.20 g (1 mmol) of 1-methylperimidinone **VII**, 0.27 g (1.3 mmol) of 1,3-diphenyl-2-propenone, and 5 g of polyphosphoric acid was stirred for 1.5 h at 65°C. The mixture was poured into 50 ml of water, neutralized with aqueous ammonia to pH ≈ 8, and extracted with ethyl acetate (3×30 ml). The extract was dried over sodium sulfate, filtered, evaporated until it became turbid, and cooled. The precipitate was filtered off and dried. Yield 0.12 g (30%), mp 262–264°C (from ethyl acetate). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.03 s (3H, NMe), 7.60 m (10H, $2C_6H_5$), 7.63 d (1H, 9-H, $J_{9,10}$ = 9.4 Hz), 7.49 d (1H, 5-H, $J_{5,4}$ = 9.4 Hz), 7.88 s (1H, 7-H), 8.60 d (1H,

4-H, $J_{4,5}$ = 9.4 Hz), 8.32 d (1H, 10-H, $J_{10,9}$ = 9.4 Hz), 10.29 s (1H, 2-H). Mass spectrum, *m/z* (I_{rel}, %): 386 $[M]^+$ (26), 387 $[M + 1]^+$ (7), 357 $[M - H_2C{=}NH]^+$ (44). Found, %: C 83.79; H 4.76; N 7.20. $C_{27}H_{18}N_2O$. Calculated, %: C 83.92; H 4.69; N 7.25.

1,3-Dimethyl-2-oxo-6,8-diphenyl-1,2-dihydro-1,3-diazapyrenium iodide (XVIb). A mixture of 0.38 g (1 mmol) of compound **XIVb** and 0.19 ml (3 mmol) of methyl iodide in 20 ml of acetonitrile was heated for 4 h under reflux. The solution was evaporated to a volume of 3 ml, and 10–15 ml of petroleum ether was added. An oily material separated and slowly crystallized. It was separated from the solution by decanting, ground (after solidification), and heated in 20 ml of boiling ethyl acetate. The precipitate was filtered off and washed with petroleum ether. Yield 0.39 g (76%), dark violet crystals, mp 268–270°C (from acetone). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.10 s (6H, 2NMe), 7.70 m (6H, *m*-H, *p*-H), 7.80 m (4H, *o*-H), 8.29 s (1H, 7-H), 8.37 d (2H, 4-H, 10-H), 8.97 d (2H, 5-H, 9-H), $J_{4,5}$ = 9.3 Hz). Found, %: C 63.35; H 3.95; N 5.58. $C_{28}H_{21}N_2IO$. Calculated, %: C 63.65; H 4.01; N 5.30.

1,3-Dimethyl-2-oxo-6,8-diphenyl-1,2-dihydro-1,3-diazapyrenium perchlorate (XVIa). *a*. A mixture of 0.42 g (2 mmol) of 1,3-dimethylperimidinone **XV**, 0.64 g (3 mmol) of 1,3-diphenyl-2-propenone, and 6 g of polyphosphoric acid was stirred for 4 h at 65–70°C. The mixture was poured under vigorous stirring into 20 ml of 30% perchloric acid and then into 50 ml of water, and the precipitate was filtered off and washed with water. Yield 0.88 g (85%), yellow–green crystals, mp 296–298°C (from alcohol).

b. A mixture of 0.2 g of iodide **XVIb** and 5 ml of 30% perchloric acid was stirred for 0.5 h at room temperature. The precipitate was filtered off, thoroughly washed with water, and dried. The yield was nearly quantitative.

***N*,*N*′-Dimethyl-9-amino-4,6-diphenyl-1*H*-phenalen-1-imine (XVII).** A mixture of 0.52 g (1 mmol) of perchlorate **XVIa** and 20 ml of a 10% solution of sodium hydroxide was stirred for 10 min at the boiling point. The mixture was cooled, and the precipitate was filtered off, washed with water, dried, and treated with 10 ml of chloroform. The solution together with the undissolved material was applied to a column charged with ~50 g of Al_2O_3, and the column was eluted with chloroform to collect the first orange–red fraction. Removal of the solvent left a red oily substance which crystallized on grinding with petroleum ether. Yield 0.27 g (72%), red crystals, mp 242–243°C (from alcohol–benzene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.35 s (6H, 2Me), 7.18 d (2H, 2H, 8-H, $J_{2(8),3(7)}$ = 9.4 Hz), 7.44 s (1H, 5-H), 7.50 m (10H, $2C_6H_5$), 7.81 d (2H, 3-H, 7-H, $J_{3(7),2(8)}$ = 9.4 Hz), 13.36 s (1H, NH). Found, %: C 86.39; H 6.05; N 7.23. $C_{27}H_{22}N_2$. Calculated, %: C 86.60; H 5.92; N 7.48.

8-Phenyl-1,3-diazapyren-6-ol (XVIII). A mixture of 0.34 g (2 mmol) of perimidine (**I**), 0.44 g (3 mmol) of 3-phenylpropynoic acid, and 5 g of polyphosphoric acid was stirred for 3 h at 120°C. The mixture was cooled to 80°C, poured into 30 ml of water, neutralized with aqueous ammonia to pH ≈ 8, and extracted with ethyl acetate (3×30 ml). The extract was evaporated to a volume of 3 ml, and the precipitate was filtered off. Yield 0.23 g (40%), orange crystals, mp 176–178°C (decomp., from xylene). The product showed no depression of the melting point on mixing with a sample prepared as described in [6].

7,9-Dimethyl-5*H*-pyrido[1,2,3-*cd*]perimidin-5-one (XIX). A mixture of 0.74 g (4 mmol) of perimidin-2-one, 0.6 ml (6 mmol) of acetylacetone, and 7 g of polyphosphoric acid was stirred for 5.5 h at 75–80°C. The mixture was poured under vigorous stirring into 50 ml of water and filtered, the filtrate was neutralized with aqueous ammonia to pH ~8–9, and the red precipitate was filtered off, washed with water, and dried. Yield 0.87 g (87%), red crystals, mp 146–147°C (decomp., from isopropyl alcohol). The product was relatively unstable, and it gradually darkened on storage. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.92 s and 3.44 s (3H each, 9-CH_3, 7-CH_3), 7.54 s (1H, 8-H), 7.58 br.d (1H, 1-H, $J_{1,2}$ = 7.6 Hz), 7.68 br.d (1H, 3-H, $J_{3,2}$ = 8.0 Hz), 7.83 d (1H, 10-H, $J_{10,11}$ = 9.2 Hz), 7.91 d.d (1H, 2-H, $J_{2,1}$ = 7.6, $J_{2,3}$ = 8.0 Hz), 7.97 d (1H, 11-H, $J_{11,10}$ = 9.2 Hz). Mass spectrum, *m/z* (I_{rel}, %): 248 $[M]^+$ (100), 249 $[M + 1]^+$ (40), 222 (28), 220 (76), 221 (38), 43 (87). Found, %: C 77.29; H 4.51; N 11.46. $C_{16}H_{12}N_2O$. Calculated, %: C 77.40; H 4.87; N 11.28.

10-Amino-2,4-dimethylbenzo[*h*]quinoline (XX). A mixture of 0.25 g (1 mmol) of compound **XIX** and 10 ml of 10% aqueous sodium hydroxide was heated for 10 min at the boiling point. The mixture was cooled, and the brown precipitate was filtered off, washed with water, and dried. Chloroform, 7 ml, was added to the dry product, and the mixture was applied to a chromatographic column charged with a small amount of Al_2O_3. The column was eluted with chloroform to collect the first pale yellow fraction. Removal of the solvent from the eluate left 0.04 g (19%) of

compound **XX**. Yellow crystals, mp 282–283°C (from benzene–petroleum ether). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.61 s and 2.75 s (3H each, 2-Me, 4-Me), 7.23 s (1H, 3-H), 7.56 br.d (1H, 7-H, $J_{7,8}$ = 7.7 Hz), 7.70 d.d (1H, 8-H, $J_{8,7}$ = 7.7, $J_{8,9}$ = 8.3 Hz), 7.81 d (1H, 5-H, $J_{5,6}$ = 9.3 Hz), 7.85 d (1H, 6-H, $J_{6,5}$ = 9.3 Hz), 8.74 d.d (1H, 9-H, $J_{9,8}$ = 8.3, $J_{9,7}$ = 1.1 Hz), 15.02 s (1H, NH···N). Found, %: C 80.79; H 6.50; N 12.34. $C_{15}H_{14}N_2$. Calculated, %: C 81.05; H 6.35; N 12.60.

10-Ethoxycarbonylamino-2,4-dimethylbenzo[*h*]-quinoline (XXI). A mixture of 0.25 g (1 mmol) of 7,9-dimethyl-5*H*-pyrido[1,2,3-*cd*]perimidin-5-one (**XIX**), 0.1 g of KOH, and 4 ml of ethanol was stirred for 2 h at room temperature. The mixture was poured into 30 ml of water, and the precipitate was filtered off, washed with water, and dried. The dry product was treated with 7 ml of chloroform, and the mixture was applied to a chromatographic column charged with a small amount of Al_2O_3. The column was eluted with chloroform to collect the first pale yellow fraction. Removal of the solvent from the eluate left 0.06 g (21%) of compound **XXI**. Pale yellow crystals, mp 85–86°C (from petroleum ether). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.31 t (3H, C**H**$_3$CH$_2$, J = 7.2 Hz), 2.64 s and 2.66 s (3H each, 4-Me, 2-Me), 4.21 q (2H, CH$_3$C**H**$_2$, J = 7.2 Hz), 7.37 s (1H, 3-H), 7.61 d (1H, 7-H, $J_{7,8}$ = 7.7 Hz), 7.65 t (1H, 8-H, $J_{8,7}$ = 7.7, $J_{8,9}$ = 7.7 Hz), 7.82 d (1H, 5-H, $J_{5,6}$ = 9.3 Hz), 7.86 d (1H, 6-H, $J_{6,5}$ = 9.3 Hz), 8.57 d.d (1H, 9-H, $J_{9,8}$ = 7.7, $J_{9,7}$ = 2.2 Hz), 14.88 s (1H, NH···N). Found, %: C 73.69; H 6.01; N 9.37. $C_{18}H_{18}N_2O_2$. Calculated, %: C 73.45; H 6.16; N 9.52.

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