Heterocyclic analogs of pleiadiene
70.* Synthesis of 6-hydroxy-1,3-diazapyrenes

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The regioselectivity of the reactions of perimidine with cinnamic acids in polyphosphoric acid (PPA) depends on the P_2O_5 content. Procedures were developed for the synthesis of 4(9)- and 6(7)-cinnamoylperimidines. Cyclization of the latter under the action of an excess of $AlBr_3$ was accompanied by dearylation to form 6-hydroxy-1,3-diazapyrene.

Key words: perimidine, acylation, alkylation, polyphosphoric acid, Friedel—Crafts reaction, cyclization, dearylation.

Derivatives of various diazapyrenes have attracted considerable recent attention due to their properties, which, among other things, are of importance for practical applications.[2—4] As part of our continuing studies on the synthesis of one such compound, *viz.*, 1,3-diazapyrene,[5,6] we examined the reactions of perimidine (**1**) with α,β-unsaturated acids in polyphosphoric acid (PPA) as a medium. By analogy with the transformations of 1,3-dialkylperimidones, thioperimidones, and 2,3-dihydroperimidines,[7] we expected that these reactions would enable us to build on the *peri* ring in one step and to obtain hydrogenated derivatives of this heterocycle.

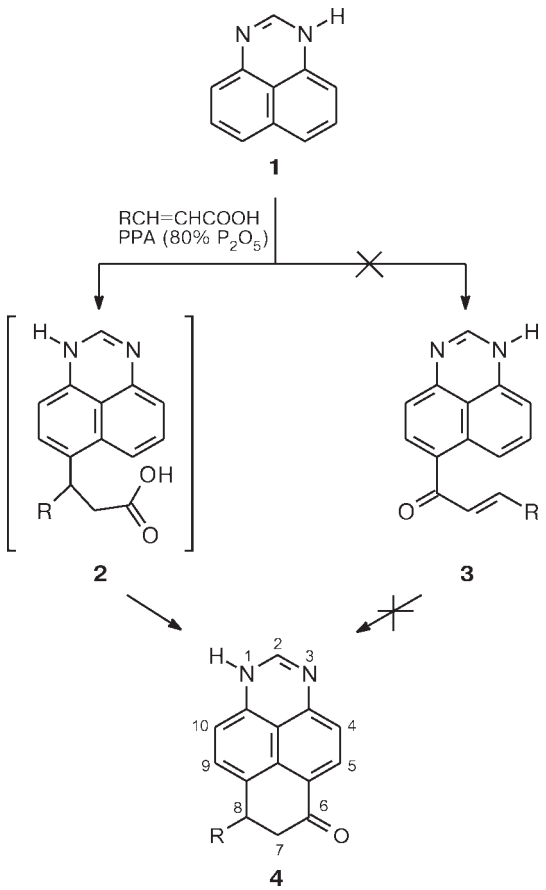
Actually, the reactions of compound **1** with cinnamic and *p*-bromocinnamic acids in standard PPA (80% of P_2O_5) proceeded even at 45—70 °C (Scheme 1) to give the corresponding 8(6)-aryl-6(8)-oxo-1,6,7,8-tetrahydro-1,3-diazapyrenes **4** as the final products.

We found that of two alternative pathways of the formation of compounds **4**, the reactions take the path involving alkylation of perimidine with the ambident cinnamoyl cation followed by intramolecular acylation of acid **2** at the *peri* position (see below).

It appeared that the direction of this reaction totally changed as the P_2O_5 content in PPA was increased to 86%, all other factors being the same, to yield (Scheme 2) 4(9)- and 6(7)-cinnamoylperimidines (**5** and **3**, respectively) with the latter product substantially predominating (for the preliminary communication, see Ref. 8).

To our knowledge, this is the first example of such an essential change in the regioselectivity of the reaction in

Scheme 1



* For Part 69, see Ref. 1.

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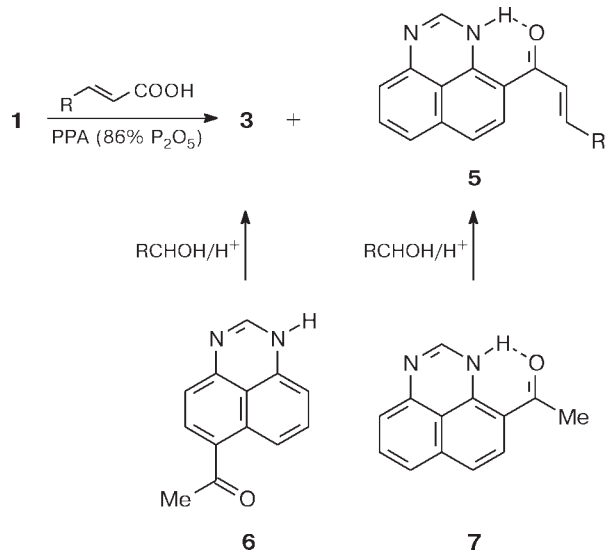
Scheme 2



R = Ph (**a**), *p*-BrC_6H_4 (**b**)

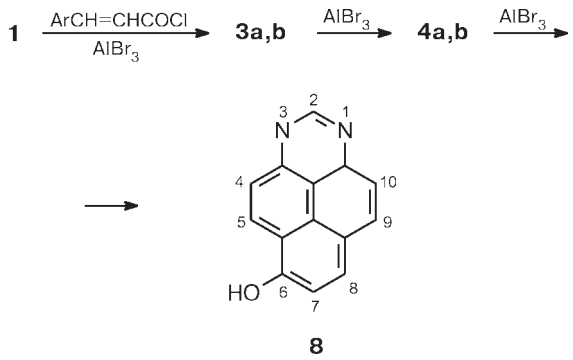
PPA depending on the P_2O_5 content. In our opinion, this is associated with the fact that the latter reaction afforded mixed anhydride of cinnamic and polyphosphoric acids, which possesses only the acylating ability.*

We also prepared cinnamoylperimidines **3** and **5** by condensation of 6(7)- (**6**) and 4(9)-acetylperimidines (**7**), respectively, with aromatic aldehydes. It should be noted that compound **3** was generated both in acidic and alkaline media, whereas compound **5** was obtained only upon acid catalysis (Scheme 2). In both cases, the reactions proceeded under rather drastic conditions (60% H_2SO_4, 75 °C or refluxing in alcoholic alkali). In our opinion, this is attributed to the fact that the formation of the enol form of ketones **6** and **7** in an acidic medium assumes double protonation (at the nitrogen and oxygen atoms), whereas the formation of enolate anion **6** requires double deprotonation.

It should be emphasized that chalcones **3** did not undergo cyclization under the conditions of their formation (60% H_2SO_4, 75 °C) as well as under the conditions of the synthesis of cyclic products **4** (80% PPA, 45—70 °C). At higher temperatures, chalcones **3** underwent resinification. The reaction of perimidine **1** with acrylic acid in PPA also led to complete resinification of the reaction mixture even in the presence of hydroquinone.

Hence, it was of interest to examine cinnamoylation of perimidine under the conditions of the classical Friedel—Crafts reaction. In the brief communication,[12] we have already noted that the reactions of compound **1** both with cinnamoyl and *p*-bromocinnamoyl chlorides in the presence of a large excess of $AlBr_3$ led to the formation of the same compound, *viz.*, 6-hydroxy-1,3-diazapyrene (**8**), as the final product. It was found that this transformation is an $AlBr_3$-catalyzed process, which involves acylation, intramolecular alkylation, and subsequent dearylation (Scheme 3).

Scheme 3



Ar = Ph, *p*-BrC_6H_4

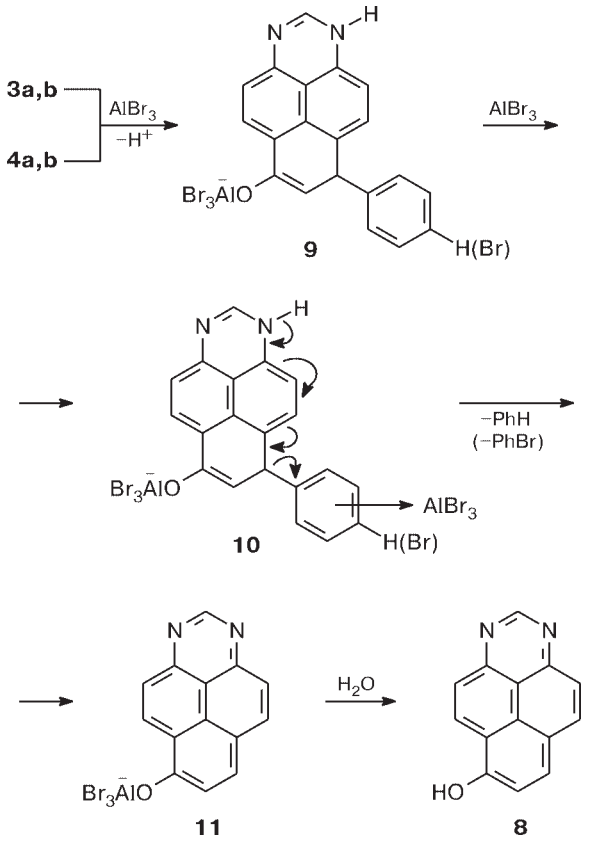
Under the same conditions, both 6(7)-cinnamoylperimidines (**3a,b**) and 8(6)-aryl-6(8)-oxo-1,6,7,8-tetrahydro-1,3-diazapyrenes (**4a,b**) produced compound **8**. Hence, the use of strong Lewis acid made it possible to perform intramolecular cyclization of compounds **3**, which did not proceed under the action of protic acids.

Previously, elimination of arenes has also been observed under the action of $AlCl_3$ on α-cinnamoylnaphthalenes, but attempts to isolate the intermediate cyclization products failed.[13] We believe that the key

* It has been noted[9,10] that PPA occurs as a complex mixture of mono- and polyphosphoric acids, the degree of their polymerization and the fraction of cyclic oligomers being increased as the P_2O_5 content increases. Simple calculations demonstrate that 80% PPA and 86% PPA, on the average, correspond to diphosphoric (pyrophosphoric) acid $H_4P_2O_7$ and heptaphosphoric acid $H_9P_7O_{22}$, respectively. In this connection, it seems reasonable to compare PPA with biological energy carriers, such as ADP and ATP, because these compounds share a common trait, *viz.*, contain the macroenergy phosphoanhydride bonds. The possibility of the transfer of the phosphate groups is provided by an intermediate position of ATP on the thermodynamic scale, which reflects the standard free energies of hydrolysis ($\Delta G°$) of different biologically important phosphates. For example, the energy $\Delta G°$ of acetyl phosphate is higher in magnitude than $\Delta G°$ of ATP (−42.3 and −37.7 kJ mol^{-1}, respectively[11]) due to which the latter cannot phosphorylate acetic acid. To the contrary, acetyl phosphate can induce the transformation of AMP or ADP into ATP. Since 80% PPA is analogous to ADP, it is unlikely that the reactions with carboxylic acids in this acid produce acyl phosphates. Taking into account that 86% PPA, undeniably, possesses the higher phosphorylating ability than ATP, one can suggest with a fair degree of assurance that this reaction affords both acyl phosphates and acyl polyphosphates.

step of the reaction proceeds as electrophilic dealkylation of arene, the external manifestation of which is elimination of the arene molecule from the substrate (Scheme 4). This reaction is irreversible because it affords two aromatic compounds and, undoubtedly, involves the formation of "phenoxides" of type **9** and π-complexes **10**. After elimination of benzene or bromobenzene, compounds **10** are transformed into 6-hydroxy-1,3-diazapyrene (**8**) through "phenoxide" **11**. It should be noted that 4(9)-cinnamoylperimidines (**5a,b**) were not involved in analogous reactions even upon heating because electrophilic alkylation at the *ortho* position with respect to the acyl group (position 5(8) of the perimidine ring) is very hindered.

Scheme 4

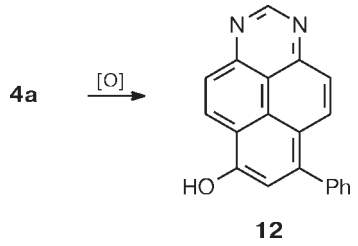


As expected, oxidation of compound **4a** with chloranil gave rise to 6-hydroxy-8-phenyl-1,3-diazapyrene (**12**).

Compounds **8** and **12** were obtained as colored crystals. These compounds possess amphoteric properties (readily soluble, in particular, in aqueous ammonia).

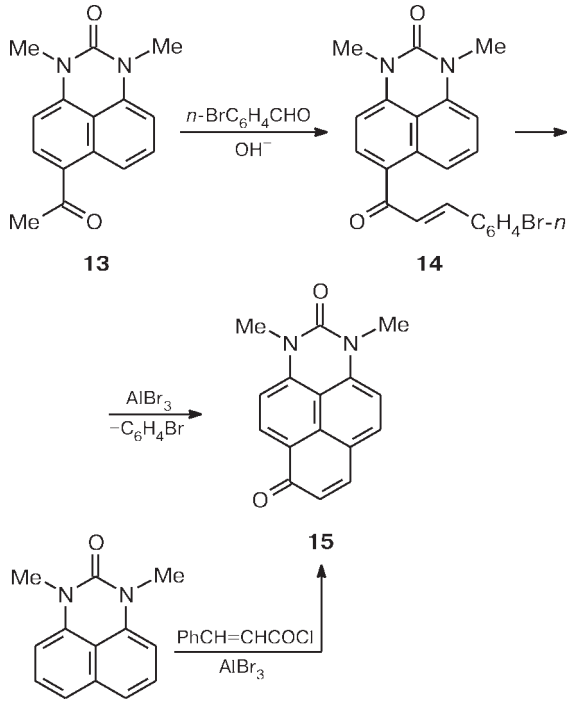
6-(*p*-Bromocinnamoyl)-1,3-dimethylperimidone (**14**) was prepared by condensation of 6-acetyl-1,3-dimethylperimidone (**13**) with *p*-bromobenzaldehyde. Under the action of an excess of $AlBr_3$, compound **14** in dichloroethane underwent transformations analogous to those

Scheme 5



described above to give 1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydro-1,3-diazapyrene (**15**). The latter was also obtained by direct acylation of 1,3-dimethylperimidone with cinnamoyl chloride (Scheme 6). Earlier, we have synthesized this compound according to another procedure.[7]

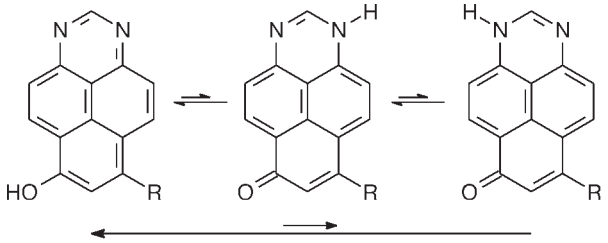
Scheme 6



Compounds **8** and **12** would be expected to occur in solutions as three tautomeric forms (Scheme 7). In this case, two NH-tautomers could be similar in properties to acylperimidines. However, judging from the spectroscopic data, these compounds exist exclusively as phenols of the 1,3-diazapyrene series both in polar (CD_3CN and DMF-d_7) and low-polarity solvents ($CDCl_3$).

Actually, the ^1H NMR spectra of compounds **8** and **12** have a singlet for the proton at the C(2) atom in the region (δ 9.67 and 9.51, respectively) identical to that in the spectrum of 1,3-diazapyrene (δ 9.75),[6] whereas this signal in the spectra of 6(7)-acetylperimidine and related

Scheme 7



cyclic products **4** is observed at substantially higher field (δ 7.4 and 7.6, respectively). The ^{13}C NMR spectrum of compound **8** has no signals characteristic of the carbonyl carbon atom. In the IR spectra of diazapyrenes **8** and **12**, absorption in the region of 1800—1600 cm^{-1} is absent (see the Experimental section).

Experimental

The ^1H NMR spectra were recorded on a Bruker WP-200 instrument with Me_4Si as the internal standard. The assignment of the signals was made using the double resonance method. The ^{13}C NMR spectra were measured on a Bruker AM-300 spectrometer (75.47 MHz). The IR spectra were recorded on a UR-20 spectrometer. The course of the reactions and the purities of the compounds were monitored on Silufol UV-254 plates. Column chromatography was carried out on silica gel Chemapol L 40—100.

Polyphosphoric acid was prepared according to a standard procedure;[14] PPA containing 86% of P_2O_5 is a very viscous liquid and it is necessary to heat this acid before use to improve its consistency. This acid, unlike samples containing 80—84% of P_2O_5, does not crystallize even upon prolonged storage.

Reaction in PPA (general procedure *A*). A mixture of perimidine (5 mmol), cinnamic or *p*-bromocinnamic acid (7.5 mmol), and PPA (10—12 g) with the corresponding P_2O_5 content was stirred at 45—50 °C or 65—70 °C (in the case of *p*-bromocinnamic acid) for 1.5 h. Then the reaction mixture was poured into a 5% ammonia solution (100 mL) with intense stirring and cooling (ammonia was added to pH ~8 when needed). The precipitate that formed was filtered off, washed with water, and dried. When the reactions were carried out with the use of 86% PPA, isomeric compounds **3** and **5** were separated on a chromatography column with silica gel by eluting 4(9)-isomer **5** and 6(7)-isomer **3** with a 1 : 1 benzene—ethyl acetate mixture (first fraction) and ethyl acetate (second fraction), respectively. After evaporation of the solvents, the corresponding cinnamoylperimidines were obtained. Compounds **4**, which were obtained with the use of 80% PPA, were purified by recrystallization from ethyl acetate.

Condensation of acetyl derivatives of perimidine with aromatic aldehydes in an acidic medium (general procedure *B*). A mixture of the corresponding acetylperimidine (4 mmol), aromatic aldehyde (4.8 mmol), and 60% sulfuric acid (6 mL) was stirred at 75—80 °C for 2.5 h and then poured as a thin stream with intense stirring and cooling into a 5% ammonia solution (50 mL). The reaction mixture was made alkaline (to pH ~8) with ammonia if required. Cooling of the reaction mixture to room temperature afforded a red precipitate, which was filtered off, washed with water, and dried.

Condensation of 6(7)-acetylperimidine with aromatic aldehydes in an alkaline medium (general procedure *C*). A mixture of 6(7)-acetylperimidine (1 mmol), the corresponding aldehyde (1.5 mmol), KOH (5 mmol), and alcohol (5 mL) was refluxed with stirring for 4 h. Then the reaction mixture was poured into water (30 mL) and acidified with dilute hydrochloric acid to pH ~8. The precipitate that formed was filtered off, washed with water, and dried.

4(9)-Cinnamoylperimidine (5a). The yield (%) and synthetic procedure (in parentheses) were: 10 (*A*) and 54 (*B*). Orange crystals with the m.p. 194—196 °C (from a mixture of benzene and light petroleum). Mixed samples, which were prepared according to different procedures, did not give a melting point depression. ^1H NMR (acetone-d_6), δ: 7.11 (br.d, 1 H, H(4), J = 7.7 Hz); 7.15 and 8.02 (both d, 1 H each, H(7), H(8), J = 9.4 Hz); 7.37 (br.d, 1 H, H(6), J = 8.2 Hz); 7.45 (m, 3 H, *m*- and *p*-H, Ph); 7.60 (br.dd, 1 H, H(5), J_{5-4} = 7.7 Hz, J_{5-6} = 8.2 Hz); 7.80 each 8.00 (both d, 1 H each, —CH=CH—CO, J_{trans} = 15.4 Hz); 7.85 (m, 2 H, *o*-H Ph); 8.04 (s, 1 H, H(2)); 13.11 (br.s, 1 H, NH). Found (%): C, 80.69; H, 4.88; N, 9.24. $C_{20}H_{14}N_2O$. Calculated (%): C, 80.52; H, 4.73; N, 9.39.

4(9)-(*p*-Bromocinnamoyl)perimidine (5b). The yield (%) and synthetic procedure (in parentheses) were: 7 (*A*) and 57 (*B*). Bright-red crystals with the m.p. 207—209 °C (from a mixture of benzene and light petroleum). Mixed samples, which were prepared according to different procedures, did not give a melting point depression. IR (Nujol mulls), ν/cm^{-1}: 1640 (C=O); 3240 (NH). ^1H NMR (acetone-d_6), δ: 7.11 (br.d, 1 H, H(4), J = 7.7 Hz); 7.14 and 8.02 (both d, 1 H each, H(7), H(8), J = 9.3 Hz); 7.38 (br.d, 1 H, H(6), J = 7.7 Hz); 7.63 (br.dd, 1 H, H(5), J_{5-4} = 7.7 Hz, J_{5-6} = 7.7 Hz); 7.65 and 7.82 (both d, 2 H each, *p*-BrPh, J = 8.8 Hz); 7.76 and 8.06 (both d, 1 H each, —CH=CH—CO, J_{trans} = 15.4 Hz); 8.04 (br.s, 1 H, H(2)); 13.10 (br.s, 1 H, NH). Found (%): C, 63.81; H, 3.66; N, 7.39. $C_{20}H_{13}BrN_2O$. Calculated (%): C, 63.68; H, 3.47; N, 7.43.

6(7)-Cinnamoylperimidine (3a). The yield (%) and synthetic procedure (in parentheses) were: 79 (*A*), 50 (*B*), and 73 (*C*). Bright-red with the m.p. 234—235 °C (from a mixture of benzene and alcohol). Mixed samples, which were prepared according to different procedures, did not give a melting point depression. ^1H NMR (DMSO-d_6), δ: 6.53 and 8.12 (both br.d, 1 H each, H(4), H(5), J = 8.2 Hz); 6.78 (dd, 1 H, H(9), J_{9-8} = 7.44 Hz, $J_{9-7} \ll 1$ Hz); 7.39 and 7.46 (m, 4 H, H(8) and *m*-H, *p*-H Ph); 7.60 and 7.73 (both d, 1 H each, —CH=CH—CO, J_{trans} = 15.7 Hz); 7.65 (s, 1 H, H(2)); 7.79 and 7.82 (m, 2 H, *o*-H Ph); 8.41 (br.dd, 1 H, H(7), J = 8.7 Hz); 11.5 (br.s, 1 H, NH). Found (%): C, 80.69; H, 4.88; N, 9.24. $C_{20}H_{14}N_2O$. Calculated (%): C, 80.52; H, 4.73; N, 9.39.

6(7)-(*p*-Bromocinnamoyl)perimidine (3b). The yield (%) and synthetic procedure (in parentheses) were: 57 (*A*), 42 (*B*), 87 (*C*). Claret-colored crystals with the m.p. 116—118 °C (from benzene). Mixed samples, which were prepared according to different procedures, did not give a melting point depression. IR (Nujol mulls), ν/cm^{-1}: 1632 (C=O); 3440 (NH). ^1H NMR ($CDCl_3$), δ: 6.51 and 7.78 (both br.d, 1 H each, H(4), H(5), J = 7.6 Hz); 6.75 (br.d, 1 H, H(9), J_{9-8} = 7.0 Hz);

7.35 and 7.63 (both d, 1 H each, —CH=CH—CO, J_{trans} = 16.0 Hz); 7.39 (br.dd, 1 H, H(8), J_{8-9} = 7.0 Hz, J_{8-7} = 8.2 Hz); 7.46 and 7.54 (both d, 2 H each, *p*-BrPh, J = 8.8 Hz); 8.25 (d, 1 H, H(7), J_{7-8} = 8.2 Hz). ^{1}H NMR (acetone-d_6), δ: 6.58 and 8.08 (both d, 1 H each, H(4), H(5), J = 8.3 Hz); 6.84 (br.d, 1 H, H(9), J_{9-8} = 8.3 Hz); 7.42 (t, 1 H, H(8), J_{8-9} = 8.3 Hz, J_{8-7} = 8.3 Hz); 7.61 (s, 1 H, H(2)); 7.62 and 7.76 (both d, 1 H each, —CH=CH—CO, J_{trans} = 15.4 Hz); 7.64 and 7.76 (both d, 2 H each, *p*-BrPh, J = 8.3 Hz); 8.51 (br.d, 1 H, H(7), J_{7-8} = 8.8 Hz). Found (%): C, 63.72; H, 3.28; N, 7.29. $C_{20}H_{13}BrN_2O$. Calculated (%): C, 63.68; H, 3.47; N, 7.43.

6(8)-Oxo-8(6)-phenyl-1,6,7,8-tetrahydro-1,3-diazapyrene (4a). The yield (%) and synthetic procedure (in parentheses) were: 55% (*A*). Orange crystals with the m.p. 156—157 °C (from ethyl acetate). ^{1}H NMR (DMSO-d_6), δ: 2.96 (m, 2 H, CH_2(7)), 4.49 (br.t, 1 H, H(8), J = 6.4 Hz); 6.51 and 7.77 (both br.d, 1 H each, H(4), H(5), J = 8.1 Hz); 6.65 and 7.05 (both d, 1 H each, H(9), H(10), J = 7.7 Hz); 7.15 and 7.30 (both m, 5 H, Ph); 7.61 (s, 1 H, H(2)); 11.36 (br.s, 1 H, NH). Found (%): C, 80.69; H, 4.88; N, 9.24. $C_{20}H_{14}N_2O$. Calculated (%): C, 80.52; H, 4.73; N, 9.39.

***p*-Bromophenyl-6(8)-oxo-8(6)-1,6,7,8-tetrahydro-1,3-diazapyrene (4b).** The yield (%) and synthetic procedure (in parentheses) were: 61% (*A*). Yellow-orange crystals with the m.p. 168—170 °C (from ethyl acetate). ^{1}H NMR (CD_3CN), δ: 2.92 and 3.01 (both dd, 1 H each, CH_2(7), J_{gem} = 15.8 Hz, J_{cis} = 6.4 Hz, J_{trans} = 6.8 Hz); 4.49 (dd, 1 H, H(8), J_{cis} = 6.4 Hz, J_{trans} = 6.8 Hz); 6.53 and 7.83 (both d, 1 H each, H(4), H(5), J = 7.7 Hz); 6.67 and 7.05 (both d, 1 H each, H(10), H(9), J = 7.7 Hz); 7.09 and 7.43 (both d, 2 H each, *p*-BrPh, J = 8.1 Hz); 7.42 (s, 1 H, H(2)). Found (%): C, 63.50; H, 3.62; N, 7.33. $C_{20}H_{13}BrN_2O$. Calculated (%): C, 63.68; H, 3.47; N, 7.43.

6-Hydroxy-1,3-diazapyrene (8). ***A.*** A solution of cinnamoyl chloride or *p*-bromocinnamoyl chloride (2 mmol) in dichloroethane (1 mL) was added dropwise with stirring to a mixture of dichloroethane (6 mL), $AlBr_3$ (10 mmol), and perimidine (2 mmol); care was taken that the reaction mixture did not warm up above 30 °C. Then the mixture was stirred at ~20 °C for 30 min, carefully poured into water (10 mL), and cooled after which light petroleum (10 mL) was added. The precipitate that formed was filtered off and dried. The dry mixture was crushed, treated with a concentrated aqueous ammonia solution (50 mL), and filtered. The filtrate was concentrated to 5 mL. The precipitate that formed was filtered off, dissolved in ethanol (20 mL), and chromatographed through a small layer of silica gel to remove inorganic impurities, and the orange zone was eluted with alcohol. After evaporation of the solvent, compound **8** was obtained from cinnamoyl chloride and *p*-bromocinnamoyl chloride in 45% and 57% yields, respectively. The resulting samples did not give a melting point depression. Red-brown crystals with the m.p. 303—305 °C (with decomposition; from ethanol). IR (Nujol mulls), ν/cm^{-1}: 1570, 1590, 1605 (ring, C=N); 3350 (OH). ^{1}H NMR (DMF-d_7), δ: 7.84 and 8.56 (both d, 1 H each, H(7), H(8), J = 8.3 Hz); 7.99 and 8.68 (both d, 1 H each, H(10), H(9), J = 8.2 Hz); 8.12 and 9.00 (both d, 1 H each, H(4), H(5), J = 9.3 Hz); 9.63 (s, 1 H, H(2)); 12.05 (br.s, 1 H, OH). ^{1}H NMR ($CDCl_3$), δ: 7.58 and 8.30 (both d, 1 H each, H(7), H(8), J = 8.3 Hz); 8.05 and 8.46 (both d, 1 H each, H(10), H(9), J = 9.0 Hz); 8.15 and 8.92 (both d, 1 H each, H(4), H(5), J = 9.3 Hz); 9.67 (s, 1 H, H(2)). ^{13}C NMR (DMSO-d_6), δ: 95.49 (1 C); 115.35 (1 C); 115.94 (1 C); 116.88 (1 C); 121.74 (1 C); 121.83 (1 C); 123.27 (1 C); 123.41 (1 C); 130.59 (1 C); 131.67 (1 C); 135.97 (1 C); 152.89 (1 C); 154.96 (1 C); 157.71 (1 C—OH). Found (%): C, 76.48; H, 3.59; N, 12.62. $C_{14}H_8N_2O$. Calculated (%): C, 76.35; H, 3.66; N, 12.72.

B. 6(7)-Cinnamoylperimidine (**3a**) (0.3 g, 1 mmol) was added with stirring to a mixture of $AlBr_3$ (1.34 g, 5 mmol) and dichloroethane (5 mL) at ~20 °C. Then the mixture was stirred for 30 min. The subsequent isolation was carried out according to the procedure *A*. The yield was 0.08 g (36%).

C. 6(7)-(*p*-Bromocinnamoyl)perimidine (**3b**) (0.38 g, 1 mmol) was added with stirring to a mixture of $AlBr_3$ (1.34 g, 5 mmol) and dichloroethane (5 mL) at ~20 °C. Then the mixture was stirred for 30 min. The subsequent isolation was carried out according to the procedure *A*. The yield was 0.13 g (60%).

D. 6(8)-Oxo-8(6)-phenyl-1,6,7,8-tetrahydro-1,3-diazapyrene (**4a**) (0.30 g, 1 mmol) was added with stirring to a mixture of $AlBr_3$ (0.80 g, 3 mmol) and dichlroethane (5 mL) at ~20 °C. Then the mixture was stirred for 30 min. The subsequent isolation was carried out according to the procedure *A*. The yield was 0.12 g (55%).

E. *p*-Bromophenyl-6(8)-oxo-8(6)-1,6,7,8-tetrahydro-1,3-diazapyrene (**4b**) (0.38 g, 1 mmol) was added with stirring to a mixture of $AlBr_3$ (0.80 g, 3 mmol) and dichloroethane (5 mL) at ~20 °C. Then the mixture was stirred for 30 min. The subsequent isolation was carried out according to the procedure *A*. Mixed samples, which were prepared according to different procedures, did not give a melting point depression.

6-Hydroxy-8-phenyl-1,3-diazapyrene (12). A mixture of 6(8)-oxo-8(6)-phenyl-1,6,7,8-tetrahydro-1,3-diazapyrene (**4a**) (0.60 g, 2 mmol), chloranil (0.49 g, 2 mmol), and toluene (20 mL) was refluxed for 1 h. The red-brown precipitate that formed was cooled, filtered off, washed with benzene, and dried. The yield was 0.57 g (95%). Orange crystals with the m.p. 176—178 °C (with decomposition, from xylene). IR (Nujol mulls), ν/cm^{-1}: 1580, 1590, 1600 (ring, C=N), 3400 (OH). ^{1}H NMR (CD_3CN), δ: 7.60 (s, 1 H, H(7)); 7.64 (m, 5 H, Ph); 7.87 and 8.45 (both d, 1 H each, H(10), H(9), J = 9.4 Hz); 8.04 and 8.90 (both d, 1 H each, H(4), H(5), J = 9.4 Hz); 9.48 (s, 1 H, H(2)). ^{1}H NMR (DMSO-d_6), δ: 7.60 (m, 5 H, Ph); 7.61 (s, 1 H, H(7)); 7.88 and 8.38 (both d, 1 H each, H(10), H(9), J = 9.2 Hz); 8.04 and 8.91 (both d, 1 H each, H(4), H(5), J = 9.2 Hz); 9.51 (s, 1 H, H(2)). Found (%): C, 80.88; H, 4.17; N, 9.56. $C_{20}H_{12}N_2O$. Calculated (%): C, 81.07; H, 4.08; N, 9.45.

6-*p*-Bromocinnamoyl-1,3-dimethylperimidone (14). A mixture of 6-acetyl-1,3-dimethylperimidone (0.25 g, 1 mmol) and *p*-bromobenzaldehyde (0.2 g, 1.1 mmol) was dissolved in a minimum amount of ethanol (~15 mL). Then finely dispersed KOH (0.10 g) was added and the mixture was refluxed for 10 min. The precipitate that formed upon cooling was filtered off, washed with cold alcohol (5 mL), and dried. The yield was 0.35 g (83%). Yellow crystals with the m.p. 232—233 °C (from a mixture of alcohol and benzene). ^{1}H NMR ($CDCl_3$), δ: 3.49 (s, 3 H, N(1)—CH_3); 3.51 (s, 3 H, N(3)—CH_3); 6.61 and 7.90 (both d, 1 H each, H(4), H(5), J = 8.2 Hz); 6.74 (br.d, 1 H, H(9), J = 7.6 Hz); 7.34 and 7.61 (both d, 1 H each, —CH=CH—CO, J = 15.8 Hz); 7.45 and 7.52 (both d, 2 H each, *p*-BrPh, J = 8.5 Hz); 7.57 (br.t, 1 H, H(8)); 8.25 (br.d, 1 H, H(7), J = 8.6 Hz). Found (%): C, 62.48; H, 4.17; N, 6.60. $C_{22}H_{17}BrN_2O_2$. Calculated (%): C, 62.72; H, 4.07; N, 6.65.

1,3-Dimethyl-2,6-dioxo-1,2,3,6-tetrahydro-1,3-diazapyrene (15). ***A.*** A solution of cinnamoyl chloride (0.18 g, 1.1 mmol) in dichloroethane (1 mL) was added dropwise with stirring to a mixture of dichloroethane (6 mL), $AlBr_3$ (2.67 g, 10 mmol), and 1,3-dimethylperimidone (0.21 g, 1 mmol); care was taken that the reaction mixture did not warm up above 30 °C. Then the mixture was stirred at ~20 °C for 30 min and carefully poured into water (10 mL). The precipitate that formed was filtered off, dried, and dissolved in ethyl acetate (50 mL) on refluxing. The undissolved precipitate was filtered off. The filtrate was concentrated to 3 mL after which an oil formed. This oil crystallized upon the addition of methanol. The yield was 0.15 g (57%).

B. 6(7)-(*p*-Bromocinnamoyl)-1,3-dimethylperimidone (0.42 g, 1 mmol) was added with stirring to a mixture of dichloroethane (6 mL) and $AlBr_3$ (2.67 g, 10 mmol); care was taken that the reaction mixture did not warm up above 30 °C. Then the mixture was stirred at ~20 °C for 30 min and carefully poured into water (10 mL). The precipitate that formed was filtered off, dried, treated with ethyl acetate (50 mL) with refluxing, and again filtered. After evaporation of the solvent, the oil that formed crystallized upon trituration with a small amount of methanol. The yield was 0.19 g (72%).

Brown crystals with the m.p. 300—301 °C (from a mixture of xylene and alcohol).

^{1}H NMR (CD_3CN), δ: 3.63 (s, 3 H, N(1)—CH_3); 3.64 (s, 3 H, N(3)—CH_3); 6.67 and 7.89 (both d, 1 H each, H(7), H(8), J = 9.4 Hz); 7.06 and 8.03 (both d, 1 H each, H(10), H(9), J = 8.3 Hz); 7.24 and 8.65 (both d, 1 H each, H(4), H(5), J = 8.8 Hz). ^{1}H NMR (DMF-d_7), δ: 3.70 (s, 3 H, N(1)—CH_3); 3.72 (s, 3 H, N(3)—CH_3); 6.67 and 7.98 (both d, 1 H each, H(7), H(8), J = 9.4 Hz); 7.20 and 8.13 (both d, 1 H each, H(10), H(9), J = 8.3 Hz); 7.42 and 8.67 (both d, 1 H each, H(4), H(5), J = 8.8 Hz). IR ($CHCl_3$), ν/cm^{-1}: 1634 (C(6)=O); 1675 (C(2)=O). On the whole, the IR spectrum of **15** was identical with that of the sample, which we have prepared previously according to another procedure.[7] Found (%): C, 72.59; H, 4.51; N, 10.47. $C_{16}H_{12}N_2O_2$. Calculated (%): C, 72.72; H, 4.58; N, 10.60.

References

1. I. V. Borovlev, O. P. Demidov, and A. F. Pozharskii, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 132 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 139].
2. N. N. Barashkov, I. V. Korotkova, and T. V. Sakhno, *J. Lumin.*, 2000, **87—89**, 794.
3. C. Sotiriou-Leventis, Z. Mao, and A.-M. M. Rawashdeh, *J. Org. Chem.*, 2000, **65**, 6017.
4. H.-C. Becker, A. Broo, and B. Norden, *J. Phys. Chem. A*, 1997, **101**, 8853.
5. I. V. Borovlev, A. V. Aksenov, and A. F. Pozharskii, *Khim. Geterotsikl. Soedin.*, 1997, **11**, 1579 [*Chem. Heterocycl. Compd.*, 1997, **11** (Engl. Transl.)].
6. I. V. Borovlev, O. P. Demidov, and A. F. Pozharskii, *Khim. Geterotsikl. Soedin.*, 2002, № 6 [*Chem. Heterocycl. Compd.,* 2002, No. 6 (Engl. Transl.)].
7. I. V. Borovlev and A. F. Pozharskii, *Khim. Geterotsikl. Soedin.*, 1978, **6**, 833 [*Chem. Heterocycl. Compd.*, 1978, **6** (Engl. Transl.)].
8. O. P. Demidov, I. V. Borovlev, and A. F. Pozharskii, *Khim. Geterotsikl. Soedin.*, 2001, № 1, 133 [*Chem. Heterocycl. Compd.*, 2001, No. 1 (Engl. Transl.)].
9. A. L. Huhti and P. A. Gartaganis, *Can. J. Chem.*, 1956, **34**, 785.
10. E. Thilo and R. Sauer, *J. Pract. Chem.*, 1957, **4**, 324.
11. A. F. Pozharskii, A. T. Soldatenkov, and A. R. Katritzky, *Heterocycles in Life and Society*, J. Wiley and Sons, Chichester—New York, 1996.
12. I. V. Borovlev, O. P. Demidov, and A. F. Pozharskii, *Khim. Geterotsikl. Soedin.*, 2001, 1136 [*Chem. Heterocycl. Compd.,* 2001, 1046 (Engl. Transl.)].
13. G. Kalischer, E. Honold, and H.Grenne, *Chem. Z.*, 1930, **2**, 469.
14. F. Uhlig, *Angew. Chem.*, 1954, **66**, 435.

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