SYNTHESIS AND PROPERTIES OF 6-(p-TOLYL)PHENANTHRIDINES AND 5,10-DI(p-TOLYL)DIAZAPYRENES

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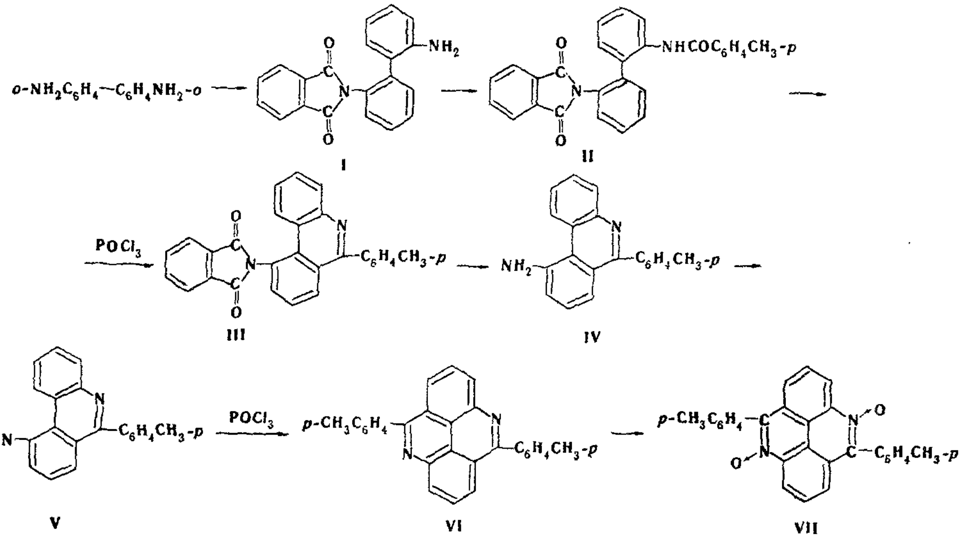
10-Amino-, 10-phthalimido-, and 10-(p-toluamido)-6-(p-tolyl)phenanthridines and 5,10-di(p-tolyl)-4,9-diazapyrene, the oxidation of which gives the 4,9-dioxide, were synthesized.

One of the methods for the preparation of derivatives of phenanthridine and 4,9-diazapyrene involves cyclodehydration of 2,2'-diacylaminodiphenyls under the influence of phosphorus oxychloride [1].

In order to obtain a heteroaromatic dicarboxylic acid that contains a 4,9-diazapyrene ring and is suitable for the preparation of polymers, we synthesized a number of new 6-(p-tolyl)phenanthridines (III-V) and 5,10-di(p-tolyl)-4,9-diazapyrenes (VI, VII).



It is known [2] that substituents (CH_3, C_6H_5) generally do not undergo oxidation during the action of chromic, perphthalic, and peracetic acids, potassium permanganate in acidic media, and sodium dichromate in glacial acetic acid on 4,9-diazapyrene and its derivatives. Oxidation of 5,10-di(p-tolyl)-4,9-diazapyrene (VI) with potassium permanganate in aqueous pyridine and with hydrogen peroxide in glacial acetic acid gave, instead of the expected diacid, 5,10-di(p-tolyl)-4,9-diazapyrene 4,9-dioxide (VII), which was identified by means of IR spectroscopy. It has been established [3] that the stretching vibrations of the NO group of heterocyclic pyridine N-oxides lie at 1230-1319 cm^{-1}, and the precise value of the frequencies depends on the degree of substitution and the nature of the substituents in the ring. In the given case, the band at 1365 cm^{-1} is characteristic for the NO group in 5,10-di(p-tolyl)-4,9-diazapyrene 4,9-dioxide. In addition, bands at 850 and 1155 cm^{-1}, which sometimes [3, 4] are also assigned to the stretching vibration of the NO group in N,N-dioxides, were also observed for this compound.

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N,N-Dioxide VII has the same properties as the analogous heterocyclic N-oxides; it does not give a color reaction with ferric chloride or with cupric acetate in ethanol [2, 5]. The starting 5,10-di(p-tolyl)-4,9-diazapyrene was obtained by reduction of VII with iron powder in the presence of glacial acetic acid or with stannous chloride in the presence of hydrochloric acid.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-10 spectrometer.

2-Amino-2'-phthalimidodiphenyl (I). This compound was obtained by the method in [6] by the action of phthalic anhydride on 2,2'-diaminodiphenyl [7].

2-(p-Toluamido)-2'-phthalimidodiphenyl (II). A mixture of 9.45 g (0.03 mole) of 2-amino-2'-phthalimidodiphenyl (I), 4.63 g (0.03 mole) of p-toluyl chloride, and 20 ml of chlorobenzene was refluxed until HCl evolution ceased. It was then cooled, and 80 ml of petroleum ether was added. The resulting precipitate was removed by filtration and washed with alcohol to give a product with mp 253-254° (from chlorobenzene) in 89% yield. Found %: C 77.5; H 4.7; N 6.5. $C_{28}H_{20}N_2O_3$. Calculated %: C 77.4; H 4.6; N 6.5. IR spectrum [8], cm^{-1}: 1375, 1450 (Ar$-CH_3$), 1525 (amide II), 1670 (Ar$-$CONH$-$), 1710, 1760 (imide ring), 1740 (1,4-Ar).

6-(p-Tolyl)-10-phthalimidophenanthridine (III). A mixture of 25.9 g (0.06 mole) of II, 46 ml (0.2 mole) of phosphorus oxychloride, and 50 ml of anhydrous nitrobenzene was refluxed for 16 h, after which it was cooled and poured over ice. The nitrobenzene was removed by steam distillation and the residue was worked up to give a product with mp 231° (from ethanol) in 85% yield. Found %: C 81.2; H 4.4; N 6.8. $C_{28}H_{18}N_2O_2$. Calculated %: C 81.1; H 4.4; N 6.8. IR spectrum, cm^{-1}: 1375, 1450 (Ar$-CH_3$); 1570, 1610 (phenanthridine ring); 1740 (1,4-Ar).

6-(p-Tolyl)-10-aminophenanthridene (IV). A 3-ml sample of 100% hydrazine hydrate was added dropwise in the course of 30 min to a refluxing solution of 8.22 g (0.02 mole) of 6-(p-tolyl)-10-phthalimidophenanthridine (III) in 60 ml of alcohol, and the resulting precipitate was removed by filtration and dissolved in dilute hydrochloric acid. Addition of solid NaOH to the acid solution gave amine IV, with mp 191-192° (from ethanol), in 96% yield. Found %: C 84.5; H 5.7; N 9.8. $C_{20}H_{16}N_2$. Calculated %: C 84.5; H 5.7; N 9.8. IR spectrum, cm^{-1}: 1370, 1450 (Ar$-CH_3$); 1570, 1610 (phenanthridene ring); 1740 (1,4-Ar); 3200, 3310, 3380 ($-NH_2$).

6-(p-Tolyl)-10-(p-toluamido)phenanthridine (V). This compound, with mp 268-269° (from ethanol), was obtained in 80% yield from 6-(p-tolyl)-10-aminophenanthridine (IV) by the method used to prepare II. Found %: C 83.6; H 5.5; N 7.0. $C_{28}H_{22}N_2O$. Calculated %: C 83.6; H 5.5; N 7.0. IR spectrum, cm^{-1}: 1370, 1450 (Ar$-CH_3$); 1570, 1610 (phenanthridine ring); 1670 (Ar$-$CONH$-$); 1740 (1,4-Ar).

5,10-Di(p-tolyl)-4,9-diazapyrene (VI). This compound, with mp 328-329° (from chlorobenzene), was obtained in 42% yield from 6-(tolyl)-10-(p-toluamido)phenanthridine (V) by the method used to prepare III. Found %: C 87.5; H 5.1; N 7.3. $C_{28}H_{20}N_2$. Calculated %: C 87.5; H 5.2; N 7.3. IR spectrum, cm^{-1}: 1370, 1450 (Ar$-CH_3$); 1335, 1445, 1475, 1565, 1635 (4,9-diazapyrene ring); 1740 (1,4-Ar).

5,10-Di(p-tolyl)-4,9-diazapyrene 4,9-Dioxide (VII). A) A mixture of 3.84 g (0.01 mole) of 5,10-di(p-tolyl)-4,9-diazapyrene (VI), 50 ml of glacial acetic acid, and 10 ml of 30% hydrogen peroxide solution was heated at 70° for 8 h. It was then cooled, and 70 ml of distilled water was added. The mixture was filtered to give 1.2 g (29%) of a yellow precipitate with mp 329-331° (dec., from chlorobenzene). Found %: C 80.9; H 4.5; N 6.8. $C_{20}H_{20}N_2O_2$. Calculated %: C 80.8; H 4.8; N 6.8. IR spectrum, cm^{-1}: 1370, 1450 (Ar$-CH_3$); 1345, 1465, 1490, 1575, 1640 (4,9-diazapyrene ring); 1740 (1,4-Ar); 850, 1155, 1365 ($\equiv N \rightarrow O$) [9].

B) A mixture of 3.84 g (0.01 mole) of 5,10-di(p-tolyl)-4,9-diazapyrene (VI), 50 ml of pyridine, and 30 ml of distilled water was heated to 70°, and 50 g of potassium permanganate was added in small portions at such a rate that the mixture boiled gently. Distilled water (20 ml) was then added, and the mixture was heated at 90° for 6 h. It was then cooled, and the pyridine was removed by steam distillation. The residue was filtered to remove the precipitated manganese dioxide, and the filtrate was evaporated to 40-50 ml. The residual solution was cooled and treated with 20% hydrochloric acid until it was weakly acidic. The resulting light-yellow precipitate was removed by filtration to give 1.1 g (28%) of a substance with mp 330-331° (dec.), which was identical to the product obtained by method A.

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