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7-AZAINDOLE DERIVATIVES

XIII. Synthesis of Benzene Ring-Substituted 1-Phenyl-4-methyl-7-azaindoles*

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Benzene-ring substituted 1-phenyl-4-methyl-7-azaindolines and 1-phenyl-4-methyl-7-azaindoles are synthesized. It is shown that introduction of para electron-donating substituents into the benzene rings of N-methylaniline and aniline facilitates their reaction with 2-chloro-3-(β-chloroethyl) pyridines to give derivatives of 1-phenyl-7-azaindolines. Electron-accepting substituents at the same position slow down reaction. A study is made of dehydrogenation of 1-phenyl-4-methyl-7-azaindolines with para substituents in the benzene ring, and it is shown that it takes place considerably more easily when these substituents are electron-donors than when they are electron-acceptors.

Previous papers in this series [2-4] describe the synthesis of 1-phenyl-7-azaindolines from various 2-chloro-3-(β-chloroethyl)- pyridines and N-alkylanilines, and also show the effect of different substituents in the pyridine ring on the course of the reaction, and on the capacity of the resultant 1-phenyl-7-azaindoline derivatives to undergo dehydrogenation to the corresponding 1-phenyl-7-azaindoles.

With a view to studying the effects on these reactions of substituents in the benzene part of the molecule, and, more particularly of substituents of an electron-donating and electron accepting character, we have carried out reactions of 2, 6-dichloro-3-(β-chloroethyl)-4-methylpyridine (trichlorocollidine) I, with various parasubstituted N-methylanilines. The substituted N-methylanilines used were p-methoxy-N-methylaniline [5], p-dimethylamino-N-methylaniline**, and p-nitro-N-methylaniline [9].

According to a previously proposed [10] mechanism of formation of azaindoline derivatives, the reaction of I with secondary amines commences by nucleophilic attack of the secondary amine at position 2 in the pyridine ring. It was natural to assume that introduction of electron-accepting para substituents into N-methylaniline, causing lowering of the basicity of the amine, would hinder reaction, and conversely that introduction of electron-donating groups at the same positions, enhancing the nucleophilicity of the compound, would facilitate synthesis of azaindoline derivatives. Actually reaction of I with p-methoxy-N-methylaniline and p-dimethylamino-N-methylaniline gave, even at 140°, high yields of 1-(p-methoxyphenyl)-4-methyl-6-chloro-7-azaindoline (II), and 1-(p-dimethylaminophenyl)-4-methyl-6-chloro-7-azaindoline (III), whereas the similar reaction of I with N-methylaniline necessitates heating at 190° [2]. p-Nitro-N-methylaniline did not react with I even at 190°, and the trichlorocollidine I was recovered unchanged.

It is of interest to note that in all cases of reaction of I with aliphatic-aromatic secondary amines there was observed neither substitution of the chlorine at position 6 in the pyridine ring nor a dehydrohalogenation side reaction leading to formation of 2, 6-dichloro-3-vinyl-4-methylpyridine.

We also observed a different effect by electron-donating and electron accepting substituents in the benzene ring in reactions of 2-chloro-3-(β-chloroethyl)-4-methylpyridine (IV) [11] with para substituted anilines, p-anisidine, p-dimethylaminoaniline, p-nitroaniline, and p-cyanoaniline [12].

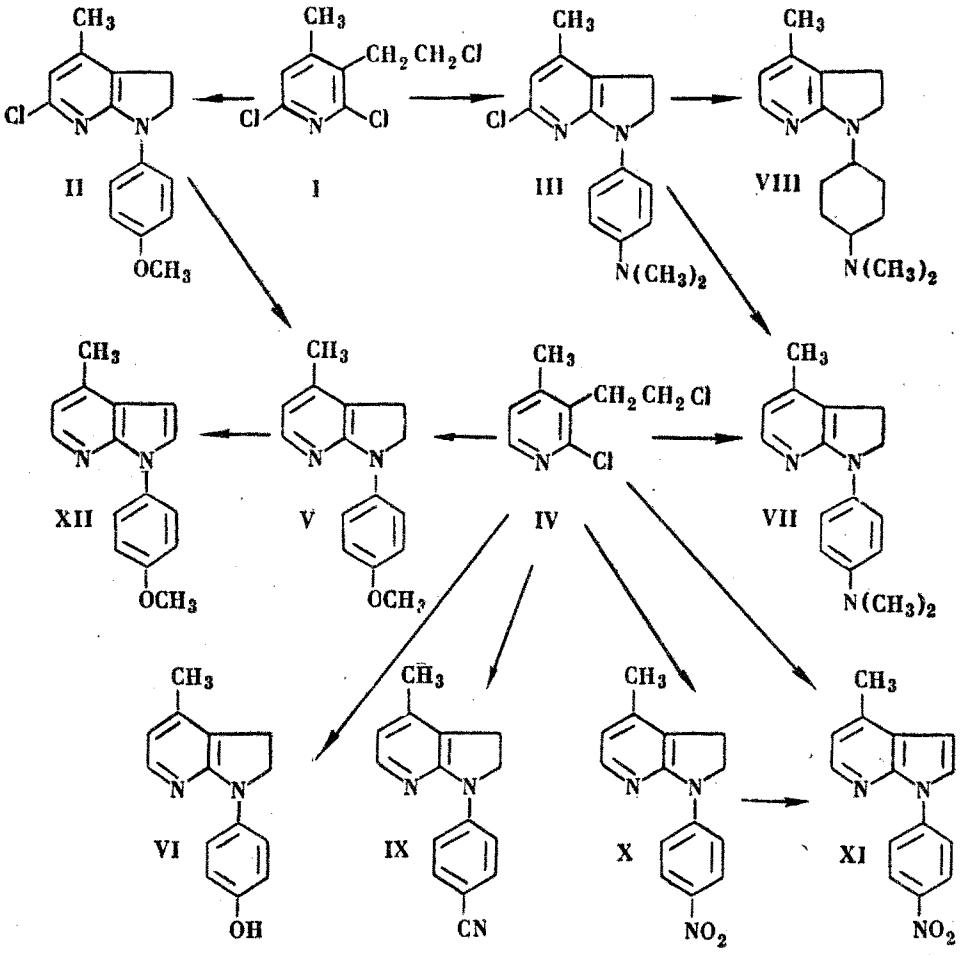
Reaction of IV with para substituted anilines under the same conditions (140°, 14 hr) gave considerably higher yields of azaindoline derivatives with electron-donating substituents (84.5% for p-anisidine, 61% for p-dimethylaminoaniline) than with electron-accepting ones (24% for p-nitroaniline, 26% for p-cyanoaniline); reaction of IV with p-nitro- and p-cyanoanilines proceeded slowly, and over 50% of IV was recovered unchanged.

1-(p-Methoxyphenyl)-4-methyl-7-azaindoline (V) and 1-(p-dimethylaminophenyl)-4-methyl-7-azaindoline (VII), made by reacting IV with p-anisidine and p-dimethylaminoaniline, were identical with the products of dehalogenation of the corresponding 6-chloro derivatives II and III. While dehalogenation of 1-(p-methoxyphenyl)-4-methyl-

* For Part XII see [1].

** p-Dimethylamino-N-methylaniline was obtained in 56.5% yield by formylating p-dimethylaminoaniline with formamide [6], followed by $LiAlH_4$ reduction of the resultant p-dimethylamino-N-formylaniline. Methods of synthesizing this compound are described in the literature. They involve dimethylation of tetramethyl-p-phenylenediamine [7] or conversion of p-dimethylaminoaniline to toluenesulfamide followed by methylation and hydrolysis of the tosyl group [8], they are more cumbrous, and give lower yields.

6-chloro-7-azaindoline (II) with palladium catalyst proceeded smoothly to give a quantitative yield of V, catalytic reduction with palladium of 1-(p-dimethylaminophenyl)-4-methyl-6-chloro-7-azaindoline (III) converted it to a mixture of amines which was difficult to separate. We succeeded in separating from it, 1-(p-dimethylaminocyclohexyl)-4-



methyl-7-azaindoline (VIII), in 21% yield, and a 3% yield of 1-(p-dimethylaminophenyl)-4-methyl-7-azaindoline (VII). As an extension of this, sodium metal in liquid ammonia was used to dehalogenate III, and gave a 64% yield of 1-(p-dimethylaminophenyl)-4-methyl-7-azaindoline (VII), reduction of the benzene ring not being observed. It is of interest to note that raising of the temperature of the reaction between IV and p-anisidine or p-nitroaniline to 190° resulted in formation of new products. With p-anisidine, saponification of the methoxyl group was observed, and the main reaction product was 1-(p-hydroxyphenyl)-4-methyl-7-azaindoline (VI), identical with the compound prepared by saponifying V with hydrochloric acid in a sealed tube at 150°. With p-nitroaniline, the 1-(p-nitrophenyl)-4-methyl-7-azaindoline (X) formed was oxidized to 1-(p-nitrophenyl)-4-methyl-7-azaindole (XI). It can be assumed, by analogy with the generally known Skraup reaction, that in this reaction the oxidizing agent is excess p-nitroaniline. In this connection it was of interest to examine the possibility of dehydrogenating 1-substituted 7-azaindolines by heating with nitrobenzene. However dehydrogenation did not take place when 1-phenyl-4-methyl-7-azaindoline was boiled for three hours with nitrobenzene, and there was quantitative recovery of the unchanged azaindoline derivative.

The effects of electron-donating and accepting substituents in the benzene ring of 1-phenyl-4-methyl-7-azaindoline on the ease of dehydrogenation of its pyrroline ring was investigated for the cases of 1-(p-nitrophenyl)-4-methyl-7-azaindoline (X) and 1-(p-methoxyphenyl)-4-methyl-7-azaindoline (V). It was found, as was to be expected, that introduction of an electron-donating substituent (methoxyl) weakened the C—H link in the pyrroline ring, and facilitated splitting off of hydrogen atoms in the dehydrogenation process. Conversely, introduction of an electron-accepting substituent (nitro group) greatly impeded dehydrogenation of the compound. Half an hour's boiling of 1-(p-methoxyphenyl)-4-methyl-7-azaindoline (V) with chloranil gave an 88% yield of 1-(p-methoxyphenyl)-4-methyl-7-azaindole (XII). In the same reaction there was 66% conversion [4] of 1-phenyl-4-methyl-7-azaindoline, while 1-(p-nitrophenyl)-4-methyl-7-azaindoline (X) was unchanged when treated with chloranil in boiling xylene. Even use of a more energetic oxidizing agent, 2, 3-dichloro-5, 6-dicyanoquinone (2 hr boiling in xylene) made it possible to effect only 20% dehydrogenation of X.

Experimental

1-(p-Methoxyphenyl)-4-methyl-6-chloro-7-azaindoline (II). 7.6 g (28 mmole) trichlorocollidine I and 9.3 g (67 mmole) p-methoxy-N-methylaniline were heated together at 140° for 14 hr. A pH 7 phosphate buffer was added to the reaction products, and the whole repeatedly extracted with benzene. The benzene extracts were dried over potash, and then distilled under reduced pressure, a cut boiling 212-220° (1 mm) being taken; yield of II, 7.45 g (80%). The material was recrystallized, to give colorless needles mp 122-123° (ex methanol), soluble in benzene, $CHCl_3$, AcOEt, Me_2CO, less soluble in ether and alcohols, insoluble in water and petrol ether. UV spectrum:* λ_{max} 236 mμ (lg ε 3.80), 289 mμ (lg ε 4.26), 334 mμ (lg ε 4.06). Found: C 65.40; H 5.53; Cl 13.05; N 10.11%. Calculated for $C_{15}H_{15}ClN_2O$: C 65.57; H 5.50; Cl 12.90; N 10.20%.

p-Dimethylamino-N-methylaniline. A mixture of 11.8 g (85 mmole) p-dimethylaminoaniline and 3.9 g (87 mmole) formamide was heated at 80° in a vacuum (20 mm) for 2 hr. The resultant p-dimethylamino-n-formylaniline obtained was recrystallized from water, and carefully dried (mass 9.6 g), then dissolved in a mixture of 250 ml dry ether and 100 ml dry dioxane, and 3.3 g $LiAlH_4$ in 100 ml dry ether added to the suspension. The reaction mixture was refluxed for 7 hr, then worked up in the usual way. The compound distilled over at 96-98° (1 mm) [7, 8], yield of p-dimethylamino-N-methylaniline 7.32 g (56.5% on the p-dimethylaminoaniline), n_D^{20} 1.5850.

1-(p-Dimethylaminophenyl)-4-methyl-6-chloro-7-azaindoline (III). 4.48 g (17 mmole) I and 6 g (44 mmole) p-dimethylamino-N-methylaniline were heated together at 140° for 14 hr. The warm reaction products were dissolved in $CHCl_3$, the resultant solution extracted first with water, then with 25% aqueous K_2CO_3 solution, after which it was dried over K_2CO_3, and distilled under reduced pressure, a cut bp 224-225° (0.5 mm) being taken. Yield of III 3.54 g (61.5%). The material was recrystallized to give colorless crystals mp 144-145° (ex ethanol), readily soluble in $CHCl_3$ and benzene, sparingly soluble in Me_2CO, AcOEt, ether, and alcohols, insoluble in water. UV spectrum: λ_{max} 242 mμ (lg ε 3.82), 297 mμ (lg ε 4.27), 340 mμ (lg ε 4.12). Found: C 66.75, 66.39; H 6.23, 6.10; Cl 12.52, 12.60; N 14.49%. Calculated for $C_{16}H_{18}ClN_3$: C 66.77; H 6.23; Cl 12.32; N 14.60%.

1-(p-Methoxyphenyl)-4-methyl-7-azaindoline (V). a) 3 g (16 mmole) IV and 3.9 g (31 mmole) p-anisidine were heated together at 140° for 14 hr. The reaction products were treated with 25% aqueous K_2CO_3, then extracted with $CHCl_3$. Distillation of the $CHCl_3$ extracts gave a cut bp 192-193° (2 mm), yield of V 3.2 g (84.5%). The material was recrystallized, to give colorless crystals mp 146-147° (ex Me_2CO), readily soluble in $CHCl_3$, less soluble in Me_2CO, benzene, AcOEt, and ether, insoluble in water and petrol ether. UV spectrum: λ_{max} 238 mμ (lg ε 3.78), 283 mμ (lg ε 4.24), 320 mμ (lg ε 3.99) (Fig. 1). R_f 0.94 (reddish-orange) (system A).** Found: C 74.82, 74.60; H 6.70, 6.34; N 11.70, 11.39%. Calculated for $C_{15}H_{16}N_2O$: C 74.97; H 6.71; N 11.66%.

The hydrochloride formed colorless crystals, mp 190-191°, undepressed mixed mp with a specimen of the hydrochloride of V prepared by method b.

b) 9g II (33 mmole) was hydrogenated in a mixture of 250 ml EtOH plus 200 ml concentrated HCl, in the presence of a palladium catalyst prepared from 5 g palladous chloride. The hydrogenation was run at room temperature, and under an excess of pressure of 20-30 cm water. The catalyst was filtered off, and the filtrate evaporated to dryness under reduced pressure. The yield of hydrochloride V was 9 g (quantitative). Colorless needles, mp 190-191°, soluble in alcohols and $CHCl_3$, insoluble in ether, Me_2CO, AcOEt, benzene, and dioxane. Found: C 65.29; H 6.21; Cl 13.01; N 10.08%. Calculated for $C_{15}H_{16}N_2O \cdot HCl$: C 65.09; H 6.19; Cl 12.81; N 10.12%.

The base prepared from V hydrochloride, had mp 146-147°, undepressed mixed mp with a specimen prepared by method a.

1-(p-Hydroxyphenyl)-4-methyl-7-azaindoline (VI). a) A solution of 1 g V hydrochloride in 10 ml concentrated HCl was heated at 150° for 12 hr in a sealed tube. The hot solution was filtered off, using carbon, and cooled. Crystals of VI hydrochloride separated, yield 0.9 g (95%). Colorless crystals mp 265-267°, readily soluble in methanol, less soluble in ethanol, Me_2CO, and $CHCl_3$, insoluble in benzene and ether. Found: Cl 13.58, 13.87; N 10.77, 10.71%. Calculated for $C_{14}H_{14}N_2O \cdot HCl$: Cl 13.50; N 10.66%.

The base VI formed colorless crystals, mp 173-175° (from AcOEt), readily soluble in MeOH and pyridine, sparingly soluble in $CHCl_3$, Me_2CO, AcOEt, and EtOH, insoluble in benzene, ether, and water. UV spectrum: λ_{max} 234 mμ (lg ε 3.75), 284 mμ (lg ε 4.23), 320 mμ (lg ε 3.94) (Fig. 1). IR spectrum: wide band 3100-3400 cm^{-1} (OH absorbing group), 1623 cm^{-1} (pyridine ring C=N), R_f 0.40 (orange) (system A). Found: C 74.03; H 6.00; N 12.32, 12.16%.

*All UV spectra were determined with a SF-4 spectrophotometer, the solvent being ethanol, while the IR spectra were observed in vaseline, with a UR-10 spectrophotometer.

**Here and in all other experiments the chromatograms were descending ones, the visualizer Dragendorff's reagent (complex color in brackets). The following solvent systems were used for chromatography: $CHCl_3$–benzene (1:1) with formamide-impregnated paper (system A), and petrol ether with the same paper (system B).

Calculated for $C_{14}H_{14}N_2O$: C 74.31; H 6.24; N 12.38%.

Attempts to hydrolyze V by boiling the concentrated HCl in an open system (18 hr) gave a mixture of 1-(p-hydroxyphenyl)-4-methyl-7-azaindoline (VI) and 1-(p-methoxyphenyl)-4-methyl-7-azaindoline (V) which was difficult to separate.

b) 3 g (16 mmole) 2-chloro-3-(β-chloroethyl)-4-methylpyridine (IV) and 3.88 g (32 mmole) p-anisidine were heated together at 190° for 7 hr. Reaction was accompanied by marked resinification; a 25% aqueous solution of K_2CO_3 was added to the reaction products, which were then extracted with $CHCl_3$, the extracts dried over K_2CO_3 and distilled under reduced pressure. A cut bp 192-198° (2 mm) was taken, mass 2.16 g. Paper chromatography (system A) showed this product to be a mixture of 1-(p-methoxyphenyl)-4-methyl-7-azaindoline, (V) (R_f 0.94) and 1-(p-hydroxyphenyl)-4-methyl-7-azaindoline (VI) (R_f 0.40), consisting mainly of VI. Quantitative separation of the mixture was difficult. A portion (0.1 g) of the mixture was chromatographed on an Al_2O_3 column (6 g Al_2O_3 was washed into a 1 cm column with benzene) and eluted with benzene, checking with system A paper chromatography. 0.025 g (14%) 1-(p-methoxyphenyl)-4-7-azaindoline (V) was obtained. The compound VI was held as its alumina derivative. 2 g mixed V and VI was recrystallized from benzene, to give 0.85 g (24%) 1-(p-hydroxyphenyl)-4-methyl-7-azaindoline (VI) mp 173-175°. Undepressed mixed mp with a specimen of VI synthesized by method a. R_f 0.40 (orange) system A). The mother liquor, containing mixed V and VI, was chromatographed on a cellulose column (2.4 g cellulose washed with petrol ether into a 1.6 cm diameter column), eluted with petrol ether, checking by system A paper chromatography. The first 200 ml eluate contained pure 1-(p-methoxyphenyl)-4-methyl-7-azaindoline (V), yield 0.23 g (6%), later portions of the eluate contained mixed IV and V (mass 0.69 g).

1-(p-Dimethylaminophenyl)-4-methyl-7-azaindoline (VII). a) A mixture of 3 g (16 mmole) IV and 4.3 g (31 mmole) p-dimethylaminoaniline was heated at 140° for 14 hr. A 25% aqueous solution of K_2CO_3 was added to the reaction products, and the mixture extracted with $CHCl_3$. The extracts were dried over K_2CO_3, and distilled under reduced pressure, a cut bp 194-195° (2 mm) being taken. Yield of VII 2.43 g (61%); recrystallization of the material gave colorless crystals, mp 153-154°, readily soluble in $CHCl_3$ and benzene, less soluble in Me_2CO, EtOAc, and alcohols, insoluble in water. UV spectrum: λ_{max} 288 mμ (lg ε 4.26), 330 mμ (lg ε 4.06) (Fig. 1). R_f 0.95 (brick red) (system A). Found: C 75.49; H 7.55; N 16.40%. Calculated for $C_{16}H_{19}N_3$: C 75.85; H 7.56; N 16.59%.

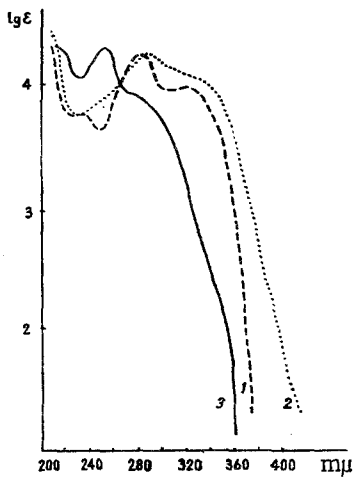


Fig. 1. UV spectra: 1) 1-(p-methoxyphenyl)-4-methyl-7-azaindoline (V) and 1-(p-hydroxyphenyl)-4-methyl-7-azaindoline (VI); 2) 1-(p-dimethylaminophenyl)-4-methyl-7-azaindoline (VII); 3) 1-(p-methoxyphenyl)-4-methyl-7-azaindole (XII).

b) 0.4 g (17 mmole) Na was added to 20 ml liquid NH_3, the mixture stirred for 5 min, then 1.2 g (~4 mmole) 1-(p-dimethylaminophenyl)-4-methyl-6-chloro-7-azaindoline (III) added. The reaction mixture was then stirred for 2 hr, 7 ml water added, the ammonia evaporated off, and VII extracted with benzene. The benzene solution was dried with K_2CO_3, and evaporated under reduced pressure. The residue (1 g) was recrystallized from ethanol, to give 0.67 g (64%) VII, mp 153-154°, undepressed mixed mp with a specimen of VII prepared by method a.

1-(p-Dimethylaminocyclohexyl)-4-methyl-7-azaindoline (VIII). 6 g palladous chloride in 30 ml boiling 17% HCl was added to a solution of 5.6 g (~ 20 mmole) 1-(p-dimethylaminophenyl)-4-methyl-6-chloro-7-azaindoline (III) in 1600 ml ethanol. The hydrogenation was run at room temperature and under an excess H_2 pressure of 20-30 cm water. The catalyst was filtered off, the filtrate evaporated under reduced pressure, the residue transformed into base by treating with 25% aqueous K_2CO_3 and then extracted with benzene. The benzene extract was dried over potash, and distilled, the following cuts being taken: 1) bp 174-177° (1 mm), 2) 177-214° (1 mm). The 1st fraction was VIII, yield 1.09 g (21%), R_f 0.00 (compound remains at the starting point) (system A). The dihydrochloride formed colorless crystals, mp 235-237°, readily soluble in alcohols, insoluble in ether and Me_2CO. Found: C 57.25; H 8.31; N 12.56%. Calculated for $C_{16}H_{25}N_3 \cdot 2HCl$: C 57.82; H 8.19; N 12.64%. From paper chromatography results (system A), the 2nd fraction (2.21 g) consisted of VIII (R_f 0.00) and a number of other amines (R_f 0.07, 0.73, and 0.85). A single crystallization from heptane followed by two from dry ether gave 0.14 g (3%) VII, mp 153-154°. Undepressed mixed mp with a specimen of VII prepared by reacting IV with p-dimethylaminoaniline.

1-(p-Cyanophenyl)-4-methyl-7-azaindoline (IX). A mixture of 2.9 g (15 mmole) IV and 3.6 g (30 mmole) p-cyanoaniline was heated at 140° for 14 hr. The reaction products were treated with 15 ml 25% aqueous K_2CO_3,

extracted with $CHCl_3$, the extracts dried over K_2CO_3, and distilled under reduced pressure, to give the cuts: 1) bp 110-115° (1 mm), 2) bp 210-230° (1 mm). The 1st cut (3.6 g) was 4 times extracted with 20 ml petrol ether each time, and the petrol ether distilled off from the total extracts, to give 1.6 g (55%) IV, bp 113-114° (4 mm), n_D^{20} 1.5535 [11]. The 2nd cut crystallized; 0.8 g (22.2%) IX was obtained, as yellowish crystals, mp 185-187° (ex ethanol), readily soluble in $CHCl_3$, sparingly soluble in Me_2CO, benzene, alcohols, and ether, UV spectrum: λ_{max} 232 mμ (lg ε 3.94), 290 mμ (lg ε 4.14), 341 mμ (lg ε 4.60) (Fig. 2); IR spectrum: 2224 cm^{-1} (C≡N), 1603 cm^{-1} (pyridine ring C=N), R_f 0.94 (yellowish-orange) (system A). Found: C 76.90; H 5.76; N 17.97%. Calculated for $C_{15}H_{13}N_3$: C 76.57; H 5.57; N 17.86%. Raising the temperature of reaction of IV with p-cyanoaniline to 190° (7 hr) raised the yield of IX to 25.6%.

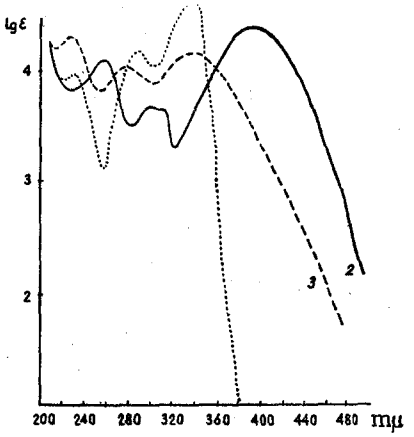


Fig. 2. UV spectra: 1) 1-(p-cyanophenyl)-4-methyl-7-azaindoline (IX); 2) 1-(p-nitrophenyl)-4-methyl-7-azaindoline (X); 3) 1-(nitrophenyl)-4-methyl-7-azaindole (XI).

1-(p-Nitrophenyl)-4-methyl-7-azaindoline (X). 3 g (16 mmole) IV and 4.35 g (~ 3 mmole) p-nitroaniline were heated together at 140° for 14 hr. The reaction products were worked up as described above for the preparation of IX. Distillation of the $CHCl_3$ solution gave the following cuts: 1) bp 110-120° (1 mm); 2) bp 210-230° (1 mm). Four extractions with petrol ether extracted from the 1st cut (2.22 g), 1.6 g (53%) IV, bp 113-114° (4 mm), n_D^{20} 1.5533 [11]. The 2nd fraction crystallized. Yield of X, 0.95 g (23.6%), yellow crystals mp 161-162° (ex ethanol), readily soluble in $CHCl_3$, sparingly soluble in benzene Me_2CO, EtOAc, alcohols, and ether, insoluble in petrol ether and water. UV spectrum: λ_{max} 260 mμ (lg ε 4.08), 302 mμ (lg ε 3.66), 314 mμ (lg ε 4.37) (Fig. 2); IR spectrum: 1598 cm^{-1} (pyridine ring C=N), 1510, 1337, 845, 754 cm^{-1} (benzene ring NO_2 group), R_f 0.94 (yellow spot; reddish-orange with Dragendorff's reagent) (system A), R_f 0.36 (system B). Found: C 65.91; H 5.13; N 16.55%. Calculated for $C_{14}H_{13}N_3O_2$: C 65.87; H 5.13; N 16.46%.

1-(p-Nitrophenyl)-4-methyl-7-azaindole (XI). a) 3 g (16 mmole) IV and 4.35 g (3 mmole) p-nitroaniline were heated together at 190° for 7 hr, as described above for the preparation of IX. Distillation of the $CHCl_3$ solution gave a cut bp 192-194° (1 mm). Yield of 1-(p-nitrophenyl)-4-methyl-7-azaindole (XI) 2.19 g (54.8%). Yellow crystals, mp 129-130° (ex ethanol), readily soluble in $CHCl_3$, sparingly soluble in Me_2CO, benzene, AcOEt, and alcohols, insoluble in water and petrol ether. UV spectrum: λ_{max} 230 mμ (lg ε 4.18), 279 mμ (lg ε 4.02), 342 mμ (lg ε 4.17) (Fig. 2). R_f 0.94 (yellow spot; with Dragendorff's reagent, reddish-orange) (system A), R_f 0.65 (system B). Found: C 66.86; H 4.35; N 16.21, 16.50%. Calculated for $C_{14}H_{11}N_3O_2$: C 66.39; H 4.38; N 16.59%.

b) A mixture of 0.1 g (0.4 mmole) X, 0.1 g (~ 0.4 mmole) 2, 3-dichloro-5, 6-dicyanoquinone and 10 ml dry xylene was refluxed for 2 hr. The dark brown precipitate formed (0.06 g) was filtered off. The xylene solution was washed 4 times with 10% aqueous NaOH, dried over K_2CO_3, and evaporated under reduced pressure. The residue (0.1 g) was recrystallized from ethanol, to give 0.03 g X, R_f 0.94 (system A), R_f 0.36 (system B), mp 155-156°. Paper chromatography (system B) showed the ethanolic mother liquor to contain a mixture of XI (R_f 0.65) and X (R_f 0.36). Column chromatography on alumina was used to separate these compounds (8 g Al_2O_3 in a column 1 cm diameter), the eluant being benzene-petrol ether (1:1) system B paper chromatography being used to check. The first 70 ml eluate contained pure XI, R_f 0.65 (system B). Evaporation under reduced pressure gave 0.02 g (20%) XI, mp 129-130°, undepressed mixed mp with a specimen of XI prepared by method a.

1-(p-Methoxyphenyl)-4-methyl-7-azaindole (XII). A mixture of 1 g (~ 4 mmole) V, 1 g (~ 8 mmole) chloranil, and 20 ml dry xylene was refluxed for 1 hr 30 min. The xylene solution was washed 4 times with 10% aqueous NaOH, dried over K_2CO_3, and evaporated under reduced pressure. The residue (0.95 g) was distilled, a cut bp 187-188° (2.5 mm) being taken. Yield of XII, 0.87 g (88%). On cooling the compound crystallized. Colorless crystals, mp 92-93°, readily soluble in benzene, xylene, and $CHCl_3$, less soluble in AcOEt, Me_2CO, ether, and alcohols, insoluble in water and petrol ether. UV spectrum: λ_{max} 235 mμ (lg ε 4.31), 282 mμ (lg ε 3.91), (Fig. 1). Found: C 75.34; H 5.78; N 11.50%. Calculated for $C_{15}H_{14}N_2O$: C 75.60; H 5.92; N 11.76%.

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