SOME PYRAZOLID-3-ONE DERIVATIVES

III. 3-Amino-1-(p-aminophenyl)-2-pyrazolines*

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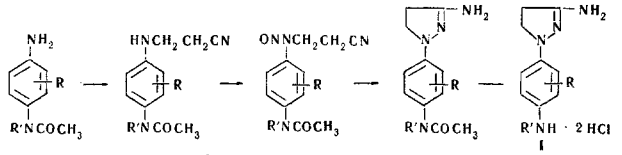
In order to study their photographic properties, a number of 3-amino-1-(p-aminophenyl)-2-pyrazolines have been synthesized from the corresponding amines.

Some 1-(p-aminophenyl)-3-iminopyrazolidines (in the tautomeric form, 3-amino-2-pyrazolines) have been patented as additives for color and black-and-white developing solutions [1]. The result of the action of these additives is a substantial increase in the level of the light-sensitivity of the photolayers treated [2].

To obtain substances of this type it has been proposed to use the reduction of the corresponding aromatic N-cyanoethyl-N-nitrosoamines [3], but their synthesis has not been described in detail.

We have synthesized a number of 3-amino-1-(p-aminophenyl)-2-pyrazolines by the following route:



Ia R=R'=H; Ib R=3-CH_3, R'=H; Ic R=H, R'=CH_3

At attempt to obtain compound I with R = 2-CH_3, R' = H proved unsuccessful. In the reduction of the N-nitroso derivative, the N—N bond was cleaved, as has been reported previously [4].

Compound **Id**, with R = H, R' = CH_3SO_2 was obtained by the route shown above starting from N-methanesulfonyl-p-phenylenediamine. During the work, the possibility of obtaining **Id** directly by the methanesulfonyl derivative for which the structure of 3-methanesulfonylamino-1-(p-methanesulfonylaminophenyl)-2-pyrazoline has been proposed.

The 3-amino-1-(p-aminophenyl)-2-pyrazolines synthesized have been tested as additives in black-and-white developers. The results of these tests will be reported separately.

EXPERIMENTAL

5-Acetamido-2-aminotoluene (II). A suspension of 50 g of 3-acetamido-6-nitrotoluene [5] and ~5 g Raney nickel in 0.5 ml of methanol was treated slowly, dropwise, with 40 ml of hydrazine hydrate. The mixture boiled with the copious evolution of gas. After the end of the vigorous reaction, another ~3 g of Raney nickel was added to the reaction mixture and it was boiled for 1 hr to decompose the excess of hydrazine hydrate. The solution formed was filtered hot and evaporated in vacuum to give 32.2 g (75.5%) of **II**. Colorless prisms with mp 69–70.5° C (from water). Found, %: C 62.69, 62.61; H 7.45, 7.26; N 16.21, 16.17. Calculated for $C_9H_{11}N_2O \cdot 0.5H_2O$, %: C 62.40; H 7.56; N 16.17.

N-β-Cyanoethyl-N'-methanesulfonyl-p-phenylenediamine (III). A mixture of 73.7 g of N-methanesulfonyl-p-phenylenediamine, 45 ml of acrylonitrile, and 340 ml of water was boiled for 6 hr. The precipitate that deposited on cooling was filtered off, washed with a small amount of ice water and dried in the air. This gave 65 g (68%) of substance. Colorless plates with mp 102–104° C (from water). Found, %: C 50.25, 50.14; H 5.97, 5.78; N 17.61, 17.52. Calculated for $C_{10}H_{13}N_3O_2S$, %: C 50.18; H 5.47; N 17.56.

The other cyanoethylated amides were obtained similarly (see Table 1).

N-(β-Cyanoethyl)-N'-methanesulfonyl-N-nitroso-p-phenylenediamine (IV). A solution of 100 g of **III** and 200 ml of 16% HCl was cooled to 0° C, and a solution of 29 g of sodium nitrite in 50 ml of water was added dropwise, after which the mixture was kept at 0° C for 2 hr. The precipitate that had deposited was filtered off, washed free from acid with water, and dried in the air. Yield 48.2 g (43%). Light yellow needles with mp 122° C (decomp., from aqueous methanol). Found, %: N 21.24, 20.99. Calculated for $C_{10}H_{12}N_4O_3S$, %: N 21.22.

The other nitrosoamines were obtained similarly (see Table 2).

3-Amino-1-(p-methanesulfonylaminophenyl)-2-pyrazoline (Id). A solution of 20 g of **IV** in 400 ml of glacial acetic acid at 12–15° C was treated in small portions with 36 g of zinc dust, and the mixture was stirred at 15° C for 1 hr and was left overnight at room temperature. After this, the solid matter was filtered off, the filtrate was concentrated in vacuum to small volume, and the residue was neutralized with 10% caustic soda solution. The precipitate that deposited was filtered off, washed with water, and dried at ~100° C. Yield 5 g (26.4%). Mp 182–185° C (from water). Literature data: mp 185° C.

1-(p-Acetylaminophenyl)-3-amino-2-pyrazoline. This was obtained in a similar manner to **Id**. Yield 48.7%. Colorless prisms with mp 204–206° C (from methanol). According to the literature [6], mp 204° C. On being boiled with an ethanolic solution of picric acid, it formed a **picrate**. Yellow needles with mp 186–187° C. Found, %: N 22.09, 21.86. Calculated for $C_{11}H_{14}N_4O \cdot C_6H_3N_3O_7$, %: N 21.92.

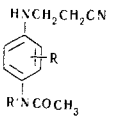
1-(4-Acetamido-3-methylphenyl)-3-amino-2-pyrazoline (V). This was obtained in a similar manner to **Id**. After the concentration of the acetic acid solution, the residue was treated with 20% sodium carbonate solution, and the precipitate was filtered off, washed with water, dried, and boiled with dry acetone. The insoluble residue was filtered off and the filtrate was evaporated to dryness. Yield 51%. Colorless prisms with mp 244–244.5° C (from aqueous methanol). Found, %: C 61.99, 61.70; H 7.41, 7.14; N 24.08, 24.18. Calculated for $C_{12}H_{16}N_4O$, %: C 62.04; H 6.94; N 24.12. **Picrate**, yellow needles with mp 204–205° C (from methanol). Found, %: N 21.49, 21.47. Calculated for $C_{12}H_{16}N_4O \cdot C_6H_3N_3O_7$, %: N 21.25.

3-Amino-1-(p-methylacetylaminophenyl)-2-pyrazoline. This was obtained in a similar manner to **Id**. Yield 39.2%. Colorless prisms with mp 232° C (from ethanol). According to the literature [3], mp 232° C.

Dihydrochloride of 3-amino-1-(4-amino-3-methylphenyl)-2-pyrazoline (Ib). This was obtained by the hydrolysis of **V** by a published method [1]. The amine liberated was filtered off and dissolved in methanol, and the solution was treated with conc. HCl. The precipitate that deposited was filtered off, washed with methanol saturated with hydrogen chloride, and dried. Yield 66%. Colorless needles (from

*For part II, see [4].

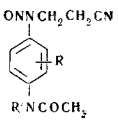
Table 1



R	R′	Reaction time, hr	Mp, °C	Form of the crystals	Empirical formula	Found, %			Calculated, %			Yield, %
						C	H	N	C	H	N	
H	H	3	121—122	Prisms	$C_{11}H_{13}N_3O$			20.91 20.64			20.67	75
2-CH_3	H	4	133.5— —135	Prisms	$C_{12}H_{15}N_3O$			19.54 19.24			19.34	19.7*
3-CH_3	H	3	104.5— —105.5	Needles	$C_{12}H_{15}N_3O\cdot H_2O$	61.29 61.15	7.06 7.36	17.81 17.71	61.25	7.28	17.90	40.5
H	CH_3	6	122	Leaflets	$C_{12}H_{15}N_3O$	66.80 66.52	6.62 6.69	19.22 19.07	66.33	6.95	19.34	41.8**

*43.5% of the initial amine was recovered from the mother solution.
**48.3% of the initial amine was recovered from the mother solution.

Table 2



R	R′	Yield, %	Mp, °C (decomp.)	Empirical formula	Found, %			Calculated, %		
					C	H	N	C	H	N
H	H	88	151—152	$C_{11}H_{12}N_4O_2$	56.92 56.72	4.98 4.87	24.08 24.48	56.88	5.20	24.12
2-CH_3	H	76*	99—100	$C_{12}H_{14}N_4O_2$			22.63 22.58			22.75
3-CH_3	H	83*	105—106				22.91 22.96			22.75
H	CH_3	63	91—93		58.25 58.03	5.78 5.47		58.52	5.73	

*After nitrosation, the substance was extracted with chloroform.

conc. HCl). The substance gradually decomposes on being heated above 150° C. Found, %: N 21.09, 21.12. Calculated for $C_{10}H_{14}N_4 \cdot 2HCl$, %: N 21.29.

Dihydrochloride of 3-amino-1-(p-aminophenyl)-2-pyrazoline (Ia). This was obtained in a similar manner to **Ib**. Yield 57%. Colorless needles (from conc. HCl). On being heated, the substance decomposes without melting. Found, %: Cl 28.13, 28.20; N 22.11, 22.13. Calculated for $C_9H_{12}N_4 \cdot 2HCl$, %: Cl 28.46; N 22.49.

Dihydrochloride of 3-amino-1-(p-methylaminophenyl)-2-pyrazoline (Ic). This was obtained in a similar manner to **Ib**. The amine isolated was dissolved in dry methanol, a current of dry hydrogen chloride was passed through the solution, and the precipitate was filtered off and dried. Yield 39.7%. Colorless needles with decomp. p. ~135° C (from methanol). Found, %: Cl 27.08, 27.22. Calculated for $C_{10}H_{14}N_4 \cdot 2HCl$, %: Cl 26.94.

3-Methanesulfonylamino-1-(p-methanesulfonylaminophenyl)-2-pyrazoline. At room temperature, 1 g of **Ia** was treated with 1.5 g of methanesulfonyl chloride, the reaction mixture was heated in the boiling water bath, the solid mass formed was dissolved in the minimum amount of ethanol, and the solution was poured into a large volume of water. The precipitate that deposited was filtered off, washed with water, and dried at ~100° C. Yield 0.7 g (37.1%). Mp 198–200° C (from water). Found, %: N 16.90, 16.87; S 19.29, 19.15. Calculated for $C_{11}H_{16}N_4O_4S_2$, %: N 16.85; S 19.29.

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