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Abstract

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ON THE DIAZOTIZATION OF 2-*p*-AMINOARYLINDONES. PREPARATION OF AZO DYES CONTAINING AN INDENE RING

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In one of our previous works it was established that the nitro derivatives of 2,3-diaryl- and 2-aryl-3-alkylindones obtained by us (^{1}) are converted in high yield into the corresponding aminoindones under the action of ferrous sulfate in an alkaline medium (^{2}). The aim of the present work was to establish suitable conditions for the diazotization of aminoindones, which would make it possible to obtain azo dyes containing an indene ring, which until now had not been obtained. Only a few azo dyes containing a hydrindene ring have been described in the literature (^{3,4}).

The usual methods of diazotization cannot be applied to aminoindones because of their weakly basic character and the poor solubility of their salts in water. We first tried to carry out diazotization in a medium of glacial acetic acid (^{5}) and to couple the presumably formed diazonium salt with β-naphthol. However, a dark-brown resinous product was obtained, which was not studied further. Experiments on diazotization in a medium of concentrated sulfuric acid in the presence of phosphoric acid (^{6}) and coupling with β-naphthol also gave a negative result. We then tried to carry out the diazotization of aminoindones in a not quite concentrated sulfuric-acid medium, using a solvent of basic character (pyridine) according to de Milt and Van Zandt (^{7}), and to couple the diazonium salt obtained with β-naphthol. From the neutral ethereal solution we isolated a dark red-violet mass with m.p. 197-199°, sparingly soluble in alcohol and insoluble in water and alkalis. Bearing in mind that β-naphthol always couples in the α-position, giving products insoluble in alkalis and sparingly soluble in organic solvents (^{8}), and taking into account the results of determination of the nitrogen content in this compound, we consider that it is benzoazonaphthol containing an indene ring, namely, *p*-(2-(3-phenylindonyl))-benzolazo-1-naphthol-(2) (I) (see Table 1). From the alkaline extract obtained in the same experiment, we isolated, along with unreacted β-naphthol, a small amount of red crystals with m.p. 281-285.5°, soluble in dilute alkali in the cold and insoluble in water. Our supposition that this product was the 2-*p*-oxyphenyl-3-phenylindone described by Kel'shchem (^{9}) was not confirmed. It turned out that these crystals contain a considerable percentage of nitrogen, corresponding to that calculated for the corresponding diazo acid of diphenylindone (X). It is known that some anti-forms of diazo acids possess considerable stability, in connection with which such a structure of the product may be regarded as probable. The above-mentioned 2-*p*-oxyphenyl-3-phenylindone was obtained by us upon decomposition of the diazonium salt of aminodiphenylindone under the described (^{10}) conditions, but at 75–80°.

In order to obtain water-soluble compounds, we tested the coupling of diazotized aminodiphenylindone with P-salt and Ash acid.

Table 1

General formula of the dyes:

$$\text{Ar(R)-indonyl} - C_6H_4{-}N{=}N{-}X$$

Compound	Ar(R)	X	m.p., °C	Yield, %	N calc., %	N found (Kjeldahl), %
I	$C_6H_4 \cdot CH_3$ with C_6H_5, C_2H_5	β-naphthol residue	197–199	52.7	6.19	6.03; 6.00
II	$C_6H_4 \cdot CH_3$ with C_6H_5, C_2H_5	β-naphthol residue	226–228	46.0	6.0	5.71; 5.76
III	$C_6H_4 \cdot CH_3$ with C_6H_5, C_2H_5	β-naphthol residue	187.5–189	48.4	6.93	6.91; 7.10
IV	$C_6H_4 \cdot CH_3$ with C_6H_5, C_2H_5	HO-n-naphthalene-SO_3Na, SO_3Na residue	–	80.2	4.27	4.34; 4.28
V	$C_6H_4 \cdot CH_3$ with C_6H_5, C_2H_5	HO-n-naphthalene-SO_3Na, SO_3Na residue	–	80.7	4.18	4.21; 4.14
VI	$C_6H_4 \cdot CH_3$ with C_6H_5, C_2H_5	HO-n-naphthalene-SO_3Na, SO_3Na residue	–	70.0	4.60	4.55; 4.67

Compound	Ar(R)	X	m.p., °C	Yield, %	N calc., %	N found (Kjeldahl), %
VII	$C_6H_4 \cdot CH_3$ with C_6H_5, C_2H_5	H-acid residue: H_2N, OH, NaO_3S, SO_3Na substituted naphthalene	–	79.5	6.26	5.99; 6.06
VIII	$C_6H_4 \cdot CH_3$ with C_6H_5, C_2H_5	H-acid residue: H_2N, OH, NaO_3S, SO_3Na substituted naphthalene	–	76.8	6.13	5.89; 5.90
IX	$C_6H_4 \cdot CH_3$ with C_6H_5, C_2H_5	H-acid residue: H_2N, OH, NaO_3S, SO_3Na substituted naphthalene	–	67.7	6.74	6.54; 6.48
X	C_6H_5	–OH	281–282.5	–	8.59	8.63; –

Coupling with the β-salt was carried out in a soda solution. After salting out with sodium chloride at 70°, a dark-red crystalline powder was obtained, readily soluble in water. Wool and silk are dyed by it a dark-red color. The fastness of the dyeing on wool is 5 (fastness to washing and perspiration was determined). The method of preparation, the properties, and the results of the determination of the nitrogen content in this product give us grounds to regard it as the disodium salt of *n*-(2-(3-phenylindonyl))-benzeneazo-1-naphthol-(2)-disulfonic acid-(3,6) (IV).

Coupling with H-acid was first carried out in a mineral-acid medium at pH about 2–2.5. A dark blue-violet crystalline powder was obtained, dyeing wool and silk a violet-red color. The fastness of the dyeing on wool is 5 (to washing and to perspiration). In view of the fact that H-acid couples with diazonium salts in a mineral-acid medium in position 7, we consider that this compound is the disodium salt of *n*-(2-(3-phenylindonyl))-benzeneazo-7-(8-amino)-naphthol-(1)-disulfonic acid-(3,6) (VII). Coupling of diazotized aminodiphenylindone with H-acid in an alkaline medium was also carried out. In this case a dark-violet crystalline powder, readily soluble in water, was obtained, dyeing wool and silk black with a violet shade. On the basis of the considerations set out above, we regard this compound as the disodium salt of *n*-(2-(3-phenylindonyl))-benzeneazo-2-(8-amino)-naphthol-(1)-disulfonic acid-(3,6) (XI).

From diazotized aminodiphenylindone and H-acid, the corresponding primary disazo dye was also obtained by successive coupling in mineral-acid and alkaline media. It was a black crystalline powder, for which we adopt the structure of the disodium salt of bis-(*n*-(2-(3-phenylindonyl))-benzeneazo)-2,7-(8-amino)-naphthol-(1)-disulfonic acid-(3,6) (XII). This product dyes wool and silk black with a dark-blue shade. At concentrations below 1% it dyes wool gray.

Diazotization of 2-*n*-aminophenyl-3-*n*-tolylindone proceeded analogously. On coupling the diazonium salt with β-naphthol, *n*-(2-(3-*p*-tolylindonyl))-benzolazo-1-naphthol-(2) (II) with properties analogous to those of I. On coupling with P-salt and H-acid, products similar to those described above were obtained; for these we assign the structures of the disodium salts of *p*-(2-(3-*p*-tolylindonyl))-benzolazo-1-naphthol-(2)-disulfonic acid-(3, 6) (V) and *p*(2-(3-*p*-tolylindonyl))-benzolazo-7-(8-amino)-naphthol-(1)-disulfonic acid-(3, 6) (VIII).

[structural formula of compound XII]

The diazonium salt of 2-*p*-aminophenyl-3-ethylindone was obtained by an analogous method. On coupling with β-naphthol it gave *p*-(2-(3-ethylindonyl))-benzolazo-1-naphthol-(2) (III), and with P-salt and H-acid the disodium salts of *p*-(2-(3-ethylindonyl))-benzolazo-1-naphthol-(2)-disulfonic acid-(3, 6) (VI) and *p*-(2-3-ethylindonyl))-benzolazo-7-(8-amino)-naphthol-(1)-disulfonic acid-(3, 6) (IX).

Experimental Part

1. Coupling of aminoindones with β-naphthol. 0.310-0.414 g (0.0015 g-mol, in 3-4-fold excess) of ground sodium nitrite was dissolved in a mixture of

14 ml of conc. sulfuric acid and 7 ml of water with heating to 70°. After cooling to 10°, with continuous vigorous stirring, a solution of 0.446 g (0.0015 g-mol) of aminodiphenylindone in 10 ml of pyridine was added dropwise. During this, the temperature must not rise above 10°. After stirring for 1 hour, the mixture was diluted with twice its volume (62 ml) of ice water and 2 g of urea was added. To the resulting almost clear orange-red solution, at the same temperature, a solution of 0.227 g (0.0015 g-mol + 5% excess) of β-naphthol in 10 ml of pyridine was added, and the mixture was alkalized with dilute alkali solution. After one hour the mixture was acidified with dilute sulfuric acid and extracted with ether. The violet-red ether solution was treated successively with 18% hydrochloric acid and dilute alkali. After distilling off the ether from the neutral solution, 0.358 g of dark red-violet crystals with m.p. 197–199° (from alcohol) (I) was obtained. They are insoluble in water and alkalies and poorly soluble in alcohol, and much better in benzene and acetone. From the alkaline extracts, after acidification and extraction with ether, 0.270 g of acidic products was obtained, from which, after washing with 10 ml of ether, 0.021 g of red crystals with m.p. 281–292.5° (X) was isolated. From the acidic extracts, 0.039 g of products of basic character was isolated.

Analogously, from 0.467 g of aminophenyltolylindone, 0.322 g of violet-red crystals with m.p. 226–228° (from alcohol) (II) was obtained. From the alkaline and, respectively, acidic extract in this case 0.204 g of acidic and 0.115 g of basic products were isolated. On treating the acidic products with 10 ml of ether, 0.018 g of brick-red crystals with m.p. 284–286° was isolated. Likewise, from 0.450 g of aminophenylethylindone, 0.353 g of reddish-brown crystals with m.p. 187.5–189° (from alcohol) (III) were obtained. In this case 0.280 g of acidic and 0.055 g of basic products were obtained. From the extracted alkaline product, 0.015 g of brown crystals with m.p. 275–276.5° was isolated.

2. Coupling of aminoindones with P-salt. 0.653 g (0.0015 g-mol, in 25% excess) of P-salt was dissolved in 150–200 ml of conc. sodium carbonate solution, cooled to 2–5°, and to the solution was added dropwise a solution of 0.446 g of aminodiphenylindone, diazotized by the method described above. The dye obtained was isolated by salting out

with sodium chloride (16–17 g for each 100 ml of solution) at 70° (sp. gr. of the filtrate at 20°—1.17–1.18), washed with a solution of sodium chloride of sp. gr. 1.17, dissolved in water, salted out, and filtered again under the same conditions. After drying at 100°, the dye was extracted by repeated boiling with absolute alcohol. After concentration to a small volume, 0.790 g of a dark-red crystalline powder (IV) was obtained, readily soluble in water and poorly soluble in alcohol, insoluble in benzene and ether. In an analogous experiment, from 0.234 g of aminophenyltolylindone, 0.405 g of a red crystalline powder (V) was obtained, and from 0.225 g of aminophenylethylindone, 0.388 g of a brick-red powder (VI), with properties analogous to those described above.

3. **Coupling of aminoindones with Ash acid.** 0.446 g of aminodiphenylindone was diazotized by the method described above, diluted

with ice water, and 2 g of urea was added to the solution. After this, at a temperature of 2–5° and with vigorous stirring, a solution of 0.640 g (0.0015 g-mole with a 25% excess) of Ash acid in 30 ml of water was added dropwise. The pH of the medium was brought to 2–2.5 with the aid of an aqueous solution of sodium acetate, and the mixture was stirred for another 5–6 hours at the same temperature; it is necessary that an excess of Ash acid be present in the solution (test with phenyldiazonium chloride). The dye obtained was isolated and purified by the method described above; 0.802 g of a dark blue-violet crystalline powder (VII) was obtained, similar to IV in its properties. Under the same conditions, from 0.234 g of aminophenyltolylindone, 0.395 g of a violet-blue crystalline powder (VIII) was obtained. Analogously, from 0.225 g of aminophenylethylindone, 0.380 g of a violet-red crystalline product (IX) was obtained.

4. **Preparation of product XI.** 0.640 g of Ash acid was dissolved in 150–200 ml of concentrated caustic soda solution. After this, under the conditions described in experiment 2, the diazonium solution obtained from 0.446 g of aminodiphenylindone was added to the solution. Isolation of the product obtained was carried out analogously to the experiments already described. 0.855 g (yield 84.9%) of a dark-violet crystalline powder was obtained, with properties similar to those described for IV and VII.

Found, %: N 6.34; 6.26
$C_{31}H_{19}O_8N_3S_2Na_2$. Calculated, %: N 6.26

5. **Preparation of product XII.** 0.223 g (0.00075 g-mole) of aminodiphenylindone was diazotized and coupled with 0.240 g (0.00075 g-mole) of Ash acid by the method described in experiment 3. After the end of the coupling, the solution was alkalinized with sodium carbonate, and at a temperature of 2–5° a diazonium solution of 0.223 g of aminodiphenylindone was added to it. After stirring for several hours, the dye obtained was isolated by the method already described. 0.384 g (yield 52.2%) of a black crystalline powder was obtained, poorly soluble in cold water and readily soluble in hot water, sparingly soluble in alcohol and insoluble in benzene and ether. The product dissolves readily in nitrobenzene.

Found, %: N 6.98; 6.92
$C_{52}H_{31}O_9N_5S_2Na_2$. Calculated, %: N 7.15

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