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chemical scheme I II: arylazotropolone and tropoquinone hydrazone forms

Figure 1: chemical scheme I II: arylazotropolone and tropoquinone hydrazone forms

Abstract

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CHEMISTRY

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Tautomerism of ArylazotropoIones

As is known, tropolones having no substituents in position 5 readily couple with diazonium salts. The products of this reaction are usually arylazotropolones, to which structure I is assigned ([1]).

However, in studying the properties of certain arylazotropolones, we encountered several years ago such peculiarities of these compounds as were in contradiction with formula I. This led us to undertake a more thorough investigation of arylazotropolones, in the course of which we came to the conclusion that these compounds are capable of tautomeric transformations into tropoquinone hydrazones (II). The tautomerism of arylazotropolones (I) (II) discovered by us is similar in character to the analogous tautomeric transformations of 5-nitro- and 5-nitroso-tropolones ([1,2]), as well as of aromatic oxyazo compounds. The first results of the study of the tautomerism of arylazotropolones constitute the subject of the present communication.

The studies described below were carried out with a group of 5-arylazotropolones (IV), obtained by azo coupling of the corresponding tropolones (III) with diazonium salts. The tendency of these compounds to react in the tautomeric form V was first detected by us from their ability to interact readily with *o*-phenylenediamine with formation of quinoxaline derivatives (VI), which, as is known, is not characteristic of tropolones themselves; quinoxaline derivatives (VI) were obtained from arylazotropolones IVa–IVb. On the other hand, it turned out that arylazotropolones IV –IVe very readily (already on heating in CH_3OH) split off the carboxyl group situated in position 3, passing into the corresponding 5-arylazo-4-carboxymethyltropolones (VII); this reaction is not

characteristic of the original tropolone III ([3]), from which the arylazotropolones IV –IVe were obtained, but it is quite natural for the tautomeric forms V – Ve, in which the carboxyl group being split off is in the β-position to one of the carbonyl groups. Finally, it was established that, on conversion of arylazotropolones IV –IVe into the acids (VII), and also directly from the latter, neutral compounds (VIII) are readily obtained, formed as a result of heterocycle closure in the tropoquinone-hydrazone forms of arylazotropolones.* The infrared spectra of the isolated compounds indicate that they contain an α-ketol grouping (see VIII), and their tendency to form quinoxaline derivatives with o-phenylenediamine testifies to their ability to react in the tautomeric form (IX); the presence in the molecules of an amide grouping was established in the study of the infrared spectra of the quinoxaline derivatives obtained.**

* In their character these transformations are to a certain extent similar to the process of formation of quinopurpurins (X) ([4]), which, like compounds VIII, may be regarded as derivatives of the tropoquinone-hydrazone forms of arylazotropolones.

** Thus, in the spectrum of compound VIII (Ar = C_6H_5Cl-n) a band of the stretching vibration of the group $-O-H\cdots$ was found (frequency 3270 cm^{-1} in crystals and 3325 cm^{-1} in CCl_4), characteristic of α-ketols, in which the hydroxyl group is included in a system with π-electron interaction (cf. [5]). As for the amide carbonyl band, it could not be distinctly detected in the spectrum of compound VIII (Ar = C_6H_5Cl-n), but it was found (frequency 1676 cm^{-1} in crystals) in the spectrum of the quinoxaline derivative of this compound (data of D. N. Shigorina).

Data on the tropoquinonehydrazone tautomerism of arylazotropolones I II, obtained as a result of chemical study, were then confirmed by spectroscopic investigations. It is known ([6],[7]) that tautomeric transformations of aromatic oxyazo compounds, leading to the appearance in solution of their quinonehydrazone form, are accompanied by the appearance in the visible part of the absorption spectrum of a second maximum (for example, 4-phenylazonaphthol-1 has in alcoholic solution two maxima—at 470 and 410 mμ ([6])); in this case the maximum lying in the longer-wavelength region usually belongs to the quinonehydrazone form, while the maximum with the shorter wavelength corresponds to the original azoid form of the oxyazo compound. An analogous

Table 1

No.	Substance	Solvent*	λ_{max} in mμ	λ_{max} in mμ
1	4-Phenylazonaphthol-1	C_2H_5OH	410	470

No.	Substance	Solvent*	λ_{max} in mμ	λ_{max} in mμ
2	O-Methyl ether of 4-phenylazonaphthol-1	C_2H_5OH	392	
3	Methylphenylhydrazone of 1,4-naphthoquinone	C_6H_6		466
4	5-(p-Carbethoxyphenyl)-azo-4-methyltropolone	C_2H_5OH	402	500
5	5-(p-Carbethoxyphenyl)-azo-4-carbomethyltropolone	C_2H_5OH	402	495
6	p-Sulfanilamidoquinopurpurin	C_2H_5OH		502

* In preparing solutions of the arylazotropolones, they were heated to dissolve the substance for several minutes at 60–70°. The spectra of absorption of other arylazotropolones previously described in the literature, see ([8]).

IIIa: X=H, Y=CH_3
III : X=H, Y=CH_2COOH
III : X=COOH, Y=CH_3
III : X=COOH, Y=CH_2COOH

IVa Va: X=H; Y=CH_3; Ar=C_6H_4COOEt-*p*
IV V : X=H; Y=CH_2COOH; Ar=C_6H_4COOEt-*p*
IV V : X=COOH, Y=CH_3, Ar=C_6H_4COOEt-*p*
IV V : X=COOH, Y=CH_2COOH; Ar=C_6H_4COOEt-*p*
IV V : X=COOH, Y=CH_2COOH; Ar=$C_6H_4SO_2NH_2$-*p*
IV V : X=COOH, Y=CH_2COOH; Ar=C_6H_4Cl-*p*

VI
VII
VIII IX
X

picture was observed by us also in the study of the absorption spectra of alcoholic solutions of arylazotropolones, for example IVa and IV . As is evident from the data presented in Table 1 (Nos. 4 and 5), in the visible part of the spectrum of these substances there are two maxima. The maximum with the greater wavelength (495–500 mμ) is close to the corresponding maxima of 4-phenylazonaphthol-1, of its N-methyl derivative and, especially, of quinopur-

purin (X; Ar = $C_6H_4SO_2NH_2$-*p*); see Table 1, Nos. 1, 3, and 6. Consequently, this long-wavelength maximum indicates the presence in solutions of the arylazotropolones under study of the tautomeric tropoquinonehydrazone form (V). On the other hand, the maximum with the smaller wavelength (402 mμ), close to the corresponding maximum of 4-phenylazonaphthol-1 and to the maximum of its O-methyl derivative (see Nos. 1 and 2 in Table 1), corresponds to the azotropolone form IV of the arylazotropolones.

The ability of arylazotropolenes to undergo the tautomerism considered above was recently noted by Nozoe ([9]), who, as did we, found that these compounds form quinoxaline derivatives of type VI with *o*-phenylenediamine. We express our great gratitude to Prof. Nozoe for sending samples of quinopurpurins, which facilitated our spectroscopic investigations.

Experimental Part

1. Preparation of 5-arylazotropolenes (IV)

A solution of the diazotized amine is added at 5° to an alkaline solution of tropolone IIIa–IIIf ([3],[10]), the mixture is stirred for about 1 hour and acidified. The precipitate that separates is filtered off, washed with water, recrystallized, and dried in vacuo at 40°.

Compound IVa. Orange crystals from glacial CH_3COOH. M.p. 187–188° (with decomposition). Yield 75%. Found %: C 65.20; H 4.93; N 9.20. $C_{17}H_{16}O_4N_2$. Calculated %: C 65.37; H 5.16; N 8.97. Compound IVb. Brownish-red crystals from 80% CH_3COOH. M.p. 168–169° (with decomposition). Yield 61%. Found %: C 60.64; H 4.44; N 7.67. $C_{18}H_{16}O_6N_2$. Calculated %: C 60.67; H 4.52; N 7.86. Compound IVv. Dark-red crystals from glacial CH_3COOH. M.p. 179–180° (with decomposition). Yield 51%. Found %: C 60.69; H 4.52; N 7.78. $C_{18}H_{16}O_6N_2$. Calculated %: C 60.67; H 4.52; N 7.86. Compound IVg. Crystallized from 80% CH_3COOH (1 : 30), heating for 1–2 min at 30° and filtering rapidly. Brownish-red crystals with m.p. 158–159° (with decomposition). Yield 40%. Found %: C 56.79; H 3.84; N 6.63. $C_{19}H_{16}O_8N_2$. Calculated %: C 57.00; H 4.03; N 7.00*. Compound IVd. Crystallized at 30–40° analogously to compound IVg. Brownish-red crystalline hydrate with m.p. 174–175° (with decomposition); water is removed at 105–110° and 3 mm. Yield 25%. Found %: C 45.20; H 3.65; N 9.95. $C_{16}H_{16}O_8N_3S \cdot H_2O$. Calculated %: C 45.17; H 3.55; N 9.88. Compound IVe. Crystallized at 70° from glacial CH_3COOH (1 : 13) analogously to compound IVg. Brownish-red crystalline hydrate with m.p. 145–146° (with decomposition). Yield 35%. Found %: C 50.33; H 3.35; N 7.65, Cl 9.60. $C_{16}H_{11}O_6N_2Cl \cdot H_2O$. Calculated %: C 50.47; H 3.44; N 7.36; Cl 9.31.

2. Preparation of quinoxaline derivatives (VI)

A dioxane solution of the azo compound IVa–IVv and an equivalent amount of *o*-phenylenediamine is boiled for 10–12 min. The precipitate is filtered off, washed with dioxane, recrystallized, and dried at 70–80° and 1–3 mm.

Quinoxaline derivative from IVa. Dark-red crystals from glacial CH_3COOH with m.p. 243–244° (with decomposition). Yield 63%. Found %: C 69.41; H 5.33; N 13.69. $C_{23}H_{20}O_2N_4 \cdot 0.5CH_3COOH$. Calculated %: C 69.55; H 5.35; N 13.52. Quinoxaline derivative from IVb. Dark-red needles from glacial CH_3COOH with m.p. 221–222° (with decomposition). Yield 25%. **Found %: C 64.06; H 5.12; N 11.40. $C_{24}H_{20}O_4N_4 \cdot CH_3COOH$. Calculated %: C 63.92; H 4.95; N 11.47. Quinoxaline derivative from IVv. Yellow-orange crystals from dioxane with m.p. 241–242° (with decomposition). Yield 79%**. Found %: C 67.30; H 4.83; N 13.00. $C_{24}H_{20}O_4N_4$. Calculated %: C 67.28; H 4.70; N 13.08.

3. Preparation of 5-arylazotropolenes (VII) and compounds (VIII)

Decarboxylation of azo compound IVg. 2 g of IVg in 25 ml of methanol are heated for 3 hours at 60°. 91% CO_2 is split off. Without cooling, filter–

* Alkaline hydrolysis (boiling with 20% NaOH) of compound IVg leads to the formation of a series of substances of aromatic character, among which *p*-aminobenzoic acid was identified in the form of its picryl derivative; upon acid hydrolysis (boiling with 5% H_2SO_4), about 20% NH_3 is split off.

** The substance dissolves in aqueous alkalis only on heating (apparently, it contains a lactone ring).

a precipitate is separated, washed with warm methanol, and crystallized from 80% CH_3COOH. Weight 0.37 g; m.p. 168-169° (with decomposition). The substance is identical with azo compound IVb; see experiment 1. On concentrating the methanolic filtrate, compound VIII (Ar = C_6H_4COOEt-*n*) precipitates; it is washed with a solution of soda and crystallized from glacial CH_3COOH. This gives 0.12 g of long yellow needles with m.p. 231° (with decomposition). The compound is insoluble in aqueous alkalis, but is colored dark red. Before analysis the substance is dried at 50° and 3 mm. Found, %: C 63.44; H 4.19; N 7.86. $C_{18}H_{14}O_5N_2$. Calculated, %: C 63.90; H 4.17; N 8.28.

Decarboxylation of azo compound IVd. 2 g of IVd in 40 ml of 65% methanol are heated for 50 min at 60°. 96% of CO_2 is evolved. Without cooling, the precipitate is filtered off and washed with warm 65% methanol. This gives 0.44 g of azo compound VII (Ar = $C_6H_4SO_2NH_2$-*n*), which crystallizes from 80% CH_3COOH as dark-red plates with m.p. 200-201° (with decomposition). After the reaction filtrate is cooled, a second isomorphous form of the same azo compound separates (0.44 g), crystallizing from 80% CH_3COOH as thin yellow needles with m.p. 184-185° (with decomposition). Both isomorphous forms are readily converted into one another on crystallization. Yellow form: found, %: C 50.00; H 4.03; N 11.30. Red form: found, %: C 49.78; H 3.76; N 11.52. $C_{15}H_{13}O_6N_3S$. Calculated, %: C 49.58; H 3.60; N 11.56.

Decarboxylation of azo compound IVe. 3 g of IVe in 30 ml of methanol are heated for 2.5 hours at 60°. After cooling, the precipitate is filtered off, washed

with methanol, and crystallized from glacial CH_3COOH. This gives 0.17 g of compound VIII (Ar = C_6H_4Cl-*n*) as long yellow needles with m.p. 258° (with decomposition). Before analysis the substance is dried at 45° and 25 mm. Found, %: C 56.60; H 3.62; N 8.02. $C_{15}H_9O_3N_2Cl \cdot CH_3COOH$. Calculated, %: C 56.59; H 3.63; N 7.77. The crystallization acetic acid is removed at 80–85° and 3 mm.

The substance is insoluble in aqueous alkalis, but is colored dark red. On heating compound VIII (Ar = C_6H_4Cl-*n*) in dioxane solution with *o*-phenylenediamine, a quinoxaline derivative is formed with decomposition point 269–270° (from dioxane). Found, %: C 67.57; H 3.82; N 15.02. $C_{21}H_{13}ON_4Cl$. Calculated, %: C 67.65; H 3.52; N 15.03.

The reaction solution remaining after separation of compound VIII (Ar = C_6H_4Cl-*n*) is concentrated; the resulting precipitate is filtered off, washed with methanol, treated with a solution of soda, filtered again, and the filtrate is acidified. The precipitated solid is filtered off, washed with water, and crystallized from glacial CH_3COOH. This gives 0.12 g of azo compound VII (Ar = C_6H_4Cl-*n*) with m.p. 173° (with decomposition). Before analysis it is dried at 45° and 5 mm. Found, %: C 56.34; H 3.65; N 8.84. $C_{15}H_{11}O_4N_2Cl$. Calculated, %: C 56.52; H 3.48; N 8.78. On prolonged boiling in methanolic solution, the azo compound obtained gradually passes into compound VIII (Ar = C_6H_4Cl-*n*), which is isolated as described above.

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Note: Figure translations are in progress. See original paper for figures.