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Scheme 1: transformations of
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Abstract

Full Text

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ISOMERIZATION, HYDROLYTIC, AND OXIDATION-REDUCTION TRANSFORMATIONS OF 3-CARBOXY-4-CARBOXYMETHYL-5-*p*-CHLOROPHENYLAZOTROPOLONE

In continuation of the previously begun investigation of the properties of arylazotropolons (^{1}), we undertook a study of the transformations to which they may be subjected on boiling with a 20% solution of NaOH. These transformations, studied by us in detail using 3-carboxy-4-carboxymethyl-5-*p*-chlorophenylazotropolone (I) as an example, are presented in Scheme 1.

Scheme 1

It was found that under the indicated conditions arylazotropolone (I) is capable of undergoing a series of tautomeric, isomeric, hydrolytic, and oxidation–reduction transformations, ultimately leading to several compounds—(III), (VIII), (XI), (XII), and *p*-chloroaniline (VII). To isolate these substances, *p*-chloroaniline was distilled off from the reaction mixture with steam; compound (XI), which precipitated as the sodium salt during the reaction, was treated with 1 N HCl and crystallized from 50% alcohol; and compounds (III), (VIII), and (XII) were isolated by acidifying the reaction solution with H_2SO_4. After repeated extraction of the resulting precipitate with boiling ether, they were separated by fractional crystallization from 50%

CH_3COOH, alcohol, and pyridine; moreover, compound (XII) and, in part, compound (VIII) were isolated in the form of their pyridinium salts (XIV) and (XV). The structures of the substances obtained were elucidated as a result of studying their properties and transformations, and also on the basis of their IR spectra (constants and analytical data are given in Table 1)*.

Compound (III) ($C_{16}H_9O_6N_2Cl$) is a tricarboxylic acid (titration with 0.01 N

Reaction scheme: (III) → (XVI) → (XVII)

Figure 2: Reaction scheme: (III) → (XVI) → (XVII)

Reaction scheme: (XI) → (XVIII) → (XIX)

Figure 3: Reaction scheme: (XI) → (XVIII) → (XIX)

NaOH). On heating it for 2 hr in glacial AcOH, acid (XVI) and anhydride (XVII) are obtained. Study of the IR spectrum of compound (III) showed the presence in it of the carbonyl of a carboxylic acid (ν 1715 cm^{-1}) and of the $C = N$ grouping (ν 1665 cm^{-1}), whereas in the IR spectrum of anhydride (XVII) two bands were detected (at 1768 cm^{-1} and 1842 cm^{-1}), characteristic of phthalic anhydride, and a band with frequency 1636 cm^{-1}, apparently due to the $C = N$ bond [2].

Compound (XI) ($C_{15}H_9O_4N_2Cl$) is yellow, contains one carboxyl group, and has the properties of a betaine. The latter is consistent with the data of its IR spectrum, which contains a broad absorption band between 2020 and 3260 cm^{-1}, due to intramolecular interaction ($COO^- \ldots {}^+NH$), and a band with frequency 1559 cm^{-1}, characteristic of the $C—O^-$ group [2], which we have assigned to ionized carboxyl. The presence in the IR spectrum of compound (XI) of an absorption band with frequency 1625 cm^{-1} indicates the presence in it of a $C = N$ bond. On heating in pyridine or nitrobenzene, acid (XI) decarboxylates, being converted into compound (XVIII), which on heating with $Ac_2O + H_2SO_4$ forms the acetyl derivative (XIX). Compound (XVIII) exhibits amphoteric properties, forming red salts with concentrated alkalis and yellow salts with concentrated mineral acids. These salts probably possess an *o*-quinoid structure of type (XIX). The structure of compound (XVIII) and of its derivative (XIX) was confirmed by study of their IR spectra. Thus, in the acetyl derivative (XIX) a band of stretching vibrations of the carbonyl was found (ν 1749 cm^{-1}), characteristic of acylated vinyl alcohols [2], as well as an absorption band at 1613 cm^{-1}, which we have assigned to the $C = N$ bond. At the same time, in the IR spectrum of compound (XVIII) a band of stretching vibrations of the NH group was detected (ν 3287 cm^{-1}).

Compound (XII) ($C_{15}H_9O_4N_2Cl$), obtained by the action of HCl on the pyridinium salt (XIV), is yellow, has the properties of a betaine, and gives a red coloration with $FeCl_3$. The betaine structure of this compound is confirmed by the character of its IR spectrum, in which there is a broad absorption band in the region of 2530 cm^{-1}, associated with the presence of bi- of a polar ionic structure, and also a band with frequency 1558 cm^{-1}, assigned

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* The IR spectra were recorded by Yu. N. Shenker with E. M. Peresleni and I. V. Obreimov and by N. A. Chumaevskii, to whom we express our great gratitude.

structural scheme: compounds (XIV), (VIII), and (XX); (VIII) is converted by Ac_2O into (XX)

Figure 4: structural scheme: compounds (XIV), (VIII), and (XX); (VIII) is converted by Ac_2O into (XX)

to the C—O$^-$ bond (analogous bands are present in the spectrum of compound XI, which is also a betaine). Further confirmation of the structure of compound (XII) is provided by the presence in its IR spectrum of a band of stretching vibrations of a ketone carbonyl (ν 1697 cm^{-1}), a band with frequency 1634 cm^{-1} due to the C=N bond, and a broad band in the region of 3160 cm^{-1}, characteristic of a hydroxyl with a strong intramolecular hydrogen bond. As for the pyridine salt of this compound, its structure (XIV) follows from the fact that its IR spectrum contains a band of stretching vibrations of the NH group (ν 3300 cm^{-1}), as well as a band of a ketone carbonyl (ν 1707 cm^{-1}).

The last of the substances isolated by us—compound (VIII) ($C_9H_9O_5N$)—contains an enolic hydroxyl (blue coloration with $FeCl_3$) and one carboxyl group (titration with 0.01 N NaOH). This compound is capable of azo coupling with diazonium salts, but, like *o*-aminophenols, which give diazo oxides with HNO_2, it does not form diazonium salts. Distillation of compound (VIII) with zinc dust leads to the formation of a pyrrole ring (qualitative test with pine splinter), and upon heating it with Ac_2O an oxazole derivative (XX) is obtained. The tropolone nature of compound (VIII) and the character of its substituents, as well as the structure of the oxazole derivative (XX), are consistent with the results of study of their IR spectra. In the first case two bands were found (ν 1609 and 3150 cm^{-1}), characteristic of the tropolone system (^{2}), as well as a band of stretching vibrations of the OH group lying near 3600 cm^{-1}, a band of the NH group (ν 3350 cm^{-1}), and a band with frequency 1712 cm^{-1}, assigned to the carboxyl carbonyl. In the oxazole derivative (XX) two bands were found (ν 1618 cm^{-1} and 3150 cm^{-1}), indicating the presence in it of a tropolone grouping, and a band of stretching vibrations of the carbonyl of a carboxyl group (ν 1700 cm^{-1}). The presence in compound (VIII) of a tropolone system also follows from the character of its UV absorption spectrum, the intensity of whose main maxima ($\lambda_{\max}$ 260 and 330 mμ; $\lg \varepsilon$ 4.34 and 3.87), as in other tropolones, considerably exceeds the intensity of the same maxima in aromatic compounds of the benzene series (^{3,4}).

Taking into account the ability of arylazotropolones to undergo tautomeric transformations into tropoquinone hydrazones (^{1}), we believe that the compounds described above (III), (VII), (VIII), (XI), and (XII) are formed from azo compound (I) as a result of a series of transformations of its tautomeric hydrazone form (IV), represented in Scheme 1. Thus, compound (VIII) is apparently obtained as a result of decarboxylation and rearrangement of tropoquinone hydrazone (IV) into *o*-troposemidine (V), which is then hydrolyzed with elimination of *p*-chloroaniline (VII) to tropoquinone imine (VI), which is reduced to the final tropolone (VIII) by the reducing agents (II) and (IX) formed simultaneously with it. It should be noted here that the ability of tropoquinone hydrazone (IV) to undergo decarboxylation was described by us earlier (^{1}), and its rearrangement into *o*-troposemidine (V) is analogous to the known transformation of 4-phenylazonaphthol-1 into 2-anilino-1,4-naphthoquinone (^{5}).* As for compound (III), it obviously arises as a result of the usual for tropo— of aromatization of tropoquinone hydrazone (IV) into compound (II), which is then subjected to dehydrogenation cyclization under the action of a strong oxidant—tropoquinone imine (VI). The latter process is analogous to the previously known dehydrogenation cyclization of azohinoquithioles into quinopurpurins, accompanied, as in the present case, by closure of a pyrazole ring (^{6}). Finally, the formation of compounds (XI) and (XIII) probably begins with decarboxylation and hydration of tropoquinone hydrazone (IV), which leads to the hydroxo compound (IX), oxidized by tropoquinone imine (VI) to tropoquinone hydrazone (X), which is then subjected to dehydration cyclization into compound (XIII), stabilized in the form of the inner salt (XII) or aromatized into compound (XI). Dehydration cyclization of this type has already been observed by us earlier (^{1}) in other tropoquinone hydrazones of type (IV). It should be noted that the sequence of oxidation-reduction and hydrolytic transformations considered is not connected with the participation of atmospheric O_2, since identical results are obtained both in its presence and when the reaction is carried out in a nitrogen atmosphere.

Table 1

Compound	M.p., °C	Solvent	Found, % C	Found, % H	Found, % N	Found, % Cl	Calculated, % C	Calculated, % H	Calculated, % N	Calculated, % Cl
(III) · H_2O	259–261 (decomp.)	50% AcOH	50.74	2.92	7.38	9.81	50.74	2.93	7.40	9.36
(VIII)	297–298 (decomp.)	MeOH	51.45	4.29	6.89	–	51.19	4.30	6.63	–
(XI)	277–278 (decomp.)	50% EtOH	56.77	3.09	8.77	11.01	56.70	3.17	8.82	11.16
(XII)	257–258 (decomp.)	–	56.24	3.25	–	–	56.70	3.17	–	–

* It is interesting to note that the *o*-troposemidine (V) formed as an intermediate possesses the structure previously ascribed to quinopurpurins (^{7}).

Compound	M.p., °C	Solvent	Found, % C	Found, % H	Found, % N	Found, % Cl	Calculated, % C	Calculated, % H	Calculated, % N	Calculated, % Cl
(XIV)	261–262 (decomp.)	Py	60.47	3.61	10.54	9.05	60.69	3.56	10.62	8.96
(XV)	285–286 (decomp.)	Py	58.42	4.50	–	–	57.93	4.86	–	–
(XVI) • Py	264–265 (decomp.)	Py	60.55	3.60	–	8.88	60.69	3.56	–	8.96
(XVII)	263–264	Glacial AcOH	60.24	2.43	–	11.62	60.31	2.36	–	11.87
(XVIII)	282–283 (decomp.)	Glacial AcOH	61.35	3.54	10.54	12.70	61.66	3.33	10.27	13.00
(XIX)	228–230	Dioxane	60.95	3.68	8.55	–	61.06	3.52	8.90	–
(XX)	237–238 (decomp.)	EtOH	56.11	3.95	5.96	–	56.17	3.86	5.96	–

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