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TRANSFORMATIONS OF PYRROLANTHRONE-1-CARBOXYLIC ACID

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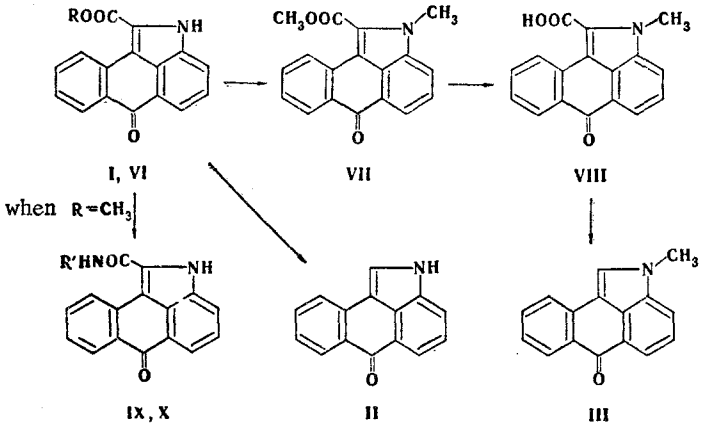
UDC 547.769.3

The preparative possibilities of syntheses based on pyrrolanthrone-1-carboxylic acid were studied. Methylation of the acid or its ester leads to N-methylpyrrolanthrone-1-carboxylic acid esters. The esters were converted to amides and hydrazides, and the latter were converted to 1-amino derivatives through the azides. The indicated transformations and decarboxylation in phosphoric acid give the products in high yields.

In a previous communication [1] we described the contraction of the heteroring in 1-diazoanthrapyridone to give pyrrolanthrone-1-carboxylic acid (I) and its esters. This transformation is the first preparative method for the synthesis of derivatives of pyrrolanthrone (6H-naphth[1,2,3-cd]indol-6-one), a heterocyclic polycondensed system that was previously difficult to obtain and has not been adequately studied. The present paper is devoted to a study of the transformations of the carboxyl group in the hope of obtaining key compounds for further syntheses — pyrrolanthrone (II), N-methylpyrrolanthrone (III), and their 1-amino derivatives (IV and V).

The action of various methylating agents (methyl iodide, diazomethane, and dimethyl sulfate) in alkaline media on acid I or its methyl ester (VI) leads to the same product — methyl N-methylpyrrolanthrone-1-carboxylate (VII), the hydrolysis of which gave the corresponding acid (VIII). Acids I and VIII, in contrast to pyrrolecarboxylic acids [2], are not capable



I R=H; VI R=CH_3; IX R'=H; X R=n-C_4H_9

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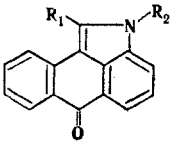
TABLE 1. Pyrrolanthrone Derivatives

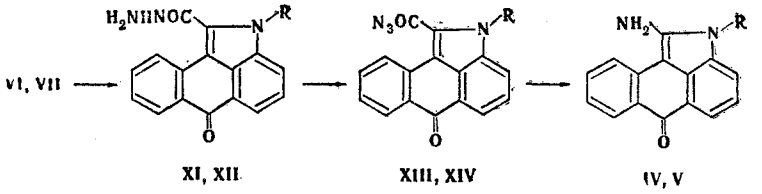


Compound	R_1	R_2	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
				C	H	N		C	H	N	
III	H	CH_3	199—200[a]	82,1	4,7	5,8	$C_{16}H_{11}NO$	82,4	4,7	6,0	79
IV	NH_2	H	Above 350[b]	77,2	4,6	11,7	$C_{15}H_{10}N_2O$	76,9	4,3	12,0	90
V	NH_2	CH_3	280—281[c]	77,7	4,9	11,5	$C_{16}H_{12}N_2O$	77,5	4,8	11,3	80
VII	$COOCH_3$	CH_3	166—167[a]	74,2	4,5	4,6	$C_{18}H_{13}NO_3$	74,2	4,5	4,8	90
VIII	COOH	CH_3	245—246 (dec.)[d]	73,9	4,0	4,8	$C_{17}H_{11}NO_3$	73,6	4,0	5,0	91
IX	$CONH_2$	H	Above 350[e]	73,6	3,9	10,7	$C_{16}H_{10}N_2O_2$	73,3	3,8	10,7	70
X	$CONHC_4H_9$	H	270—272[d]	75,5	5,7	8,8	$C_{20}H_{18}N_2O_2$	75,0	5,5	8,7	70
XI	CON_2H_3	H	Above 350[f]	69,6	3,9	14,8	$C_{16}H_{11}N_3O_2$	69,3	4,0	15,2	90
XII	CON_2H_3	CH_3	207—209[g]	69,7	4,6	14,0	$C_{17}H_{13}N_3O_2$	70,2	4,5	14,4	98

a) From benzene—hexane. b) From butanol—hexane. c) From chlorobenzene. d) From ethanol. e) From DMF. f) From DMF by the addition of water. g) From ethyl acetate by the addition of petroleum ether.

of undergoing replacement of the carboxyl group in reactions with electrophilic reagents. For example, they do not change when they are heated in acetic acid with bromine or under the influence of benzene- and 2,4-dinitrobenzenediazonium salts.

Esters VI and VII are conveniently used as the starting compounds for the synthesis of derivatives of acids I and VIII, especially since ester VI is obtained directly from 1-diazoanthrapyridone in one step [1]. They are converted to amides (for example, IX and X) and hydrazides (XI and XII) (to avoid hydrolysis of the esters the amidation should not be carried out in aqueous media). Amide IX cannot be converted to an amine by the Hofmann reaction, whereas hydrazides XI and XII smoothly undergo the Curtius rearrangement, during which all of the steps give the products in high yields (see Table 1):



IV, XI, XIII R=H; V, XII, XIV R=CH_3

Azides XIII and XIV, which are formed in 90-95% yields by the action of sodium nitrite on hydrazides XI and XII in aqueous acetic acid (in analogy with [3]), are unstable in solutions, and this makes it difficult to obtain satisfactory analytical characteristics for them. Rearrangement to amines IV and V is carried out by heating in the same medium, and the intermediate azides cannot be isolated; however, the yields and purity of the amines are reduced in this case. It is interesting that N-methylpyrrolanthrone (III) is observed in the reaction mixture in the preparation of azide XIV (R = CH_3), i.e., even at 0-5°C. In the opinion of Fischer and co-workers [3], the observed formation of 2,4-dimethylpyrrole by heating 2,4-dimethylpyrrole-5-carboxylic acid azide in dilute sulfuric acid is associated with the ease of decarboxylation of the acid itself, which is formed as a result of hydrolysis of the azide. Since acid VIII generally is difficult to decarboxylate (see below) and remains unchanged under the investigated conditions and since III is not formed simultaneously in the rearrangement of azide XIV when sodium nitrite is absent, it may be concluded that the observed transformation is the result of reaction of the azide with sodium nitrite. In fact, N-methylpyrrolanthrone (III) is obtained in 32% yield in the presence of sodium nitrite at room temperature. We have not yet been able to find similar examples in the literature, and the question of the character of this reaction remains an open one.

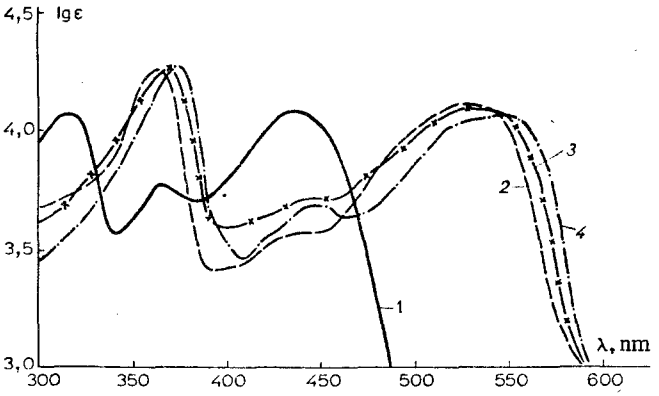


Fig. 1. Absorption spectra of N-methylpyrrolanthrone-1-carboxylic acid (VIII): 1) in acetic acid; 2) in a mixture of acetic and sulfuric acids (3:1); 3) in 85% phosphoric acid; 4) in 98% sulfuric acid.

The decarboxylation of acids I and VIII is very difficult and requires temperatures on the order of 300°C, at which destruction of the basic skeleton of the molecule, particularly cleavage of the heteroring (considerable amounts of the corresponding 1-aminoanthraquinones are observed in the pyrolysis products), occurs. At the same time, the yields of pyrrolanthrones II and III reach 70-80% when I and VIII are heated in phosphoric acid [2] to 130-160°C. Such pronounced facilitation of decarboxylation in acidic media provides a basis for the assumption that the carboxyl group is eliminated from the protonated forms of acids I and VIII, in which they exist in phosphoric acid, as seen from the spectral data (Fig. 1).

Thus the proposed method of synthesis makes it possible to easily obtain both 1-amino derivatives and pyrrolanthrones that do not contain substituents in the 1 position in high yields. This makes it expedient to investigate reactions involving substitution of pyrrolanthrone; our next communication will be devoted to this problem.

EXPERIMENTAL

The absorption spectra of the compounds were recorded with a Specord spectrometer. The yields and characteristics of the previously undescribed compounds are presented in Table 1.

Methyl N-Methylpyrrolanthrone-1-carboxylate (VII). A) A 12-ml (0.19 mole) sample of methyl iodide was added at room temperature to a solution of 5 g (0.019 mole) of acid I in 500 ml of N-methylpyrrolidone and 5.65 ml (0.0794 mole) of a 40% solution of sodium hydroxide, and the mixture was stirred for 1-2 h. It was then poured into 2.5 liters of cold water, and the precipitate was removed by filtration and chromotographed on Al_2O_3 (elution with benzene) to give ester VII.

B) Ester VII was obtained by methylation of ester VI by method A with a change in the reagent ratio of 0.018 mole of ester VI, 3.1 ml (0.0436 mole) of a 40% solution of sodium hydroxide, 0.09 mole of methyl iodide, and 250 ml of N-methylpyrrolidone.

N-Methylpyrrolanthrone-1-carboxylic Acid (VIII). A 0.25-g sample of ester VII was refluxed in 50 ml of a 1% alcohol solution of sodium hydroxide for 30 min, after which the mixture was neutralized with dilute hydrochloric acid, and the resulting precipitate was removed by filtration and washed with water to give acid VIII.

Pyrrolanthrone-1-carboxamide (IX). A 5-g sample of ester VI was heated in 100 ml of liquid ammonia at 100°C, after which the mixture was cooled, and the ammonia was evaporated to give amide IX.

N-Butylpyrrolanthrone-1-carboxamide (X). A 0.3-g sample of ester VI was refluxed in 15 ml of butylamine for 2.5 h, after which the mixture was cooled and diluted with water. The aqueous mixture was neutralized with acetic acid, and the precipitated amide X was removed by filtration.

Pyrrolanthrone-1-carboxylic Acid Hydrazides (XI, XII). A 10-g sample of ester VI or VII was heated with 40 ml of hydrazine hydrate and 100-150 ml of N-methylpyrrolidone at 50-55°C for 7 h, after which the mixture was poured into 500-750 ml of water, and the precipitated hydrazide XI or XII was removed by filtration.

Pyrrolanthrone-1-carboxylic Acid Azides (XIII, XIV). A solution of 0.028 mole of sodium nitrite in 6 ml of water was added gradually at 0-5°C to a suspension of 0.028 mole of hydrazide XI or XII in 80 ml of acetic acid and 20 ml of water, after which the mixture was stirred for 1 h. It was then diluted with 370 ml of cold water, and the resulting precipitate was removed by filtration to give 7.3 g (90%) of azide XIII [IR spectrum (KBr): 2165 cm^{-1} (N_3)] or 8 g (96%) of azide XIV [IR spectrum (KBr): 2140 cm^{-1} (N_3)].

1-Aminopyrrolanthrones (IV, V). An 8-g sample of azide XIII or XIV in 40 ml of acetic acid and 40 ml of water was heated at 80-85°C for 1-2.5 h, after which the mixture was cooled, and the resulting precipitate was removed by filtration and dried to give amine IV or V. Amine V was chromatographed on SiO_2 (40-100 mμ) (elution with chloroform and alcohol) to obtain a sample for analysis.

Pyrrolanthrone (II). A 0.5-g sample of acid I was heated in 25 ml of 85-88% phosphoric acid at 160-175°C for 2 h, after which the mixture was cooled and diluted with 125 ml of water. The aqueous mixture was neutralized with ammonium hydroxide, and the precipitate was removed by filtration, washed, dried, and chromatographed on Al_2O_3 (elution with chloroform) to give 0.29 g (70%) of pyrrolanthrone (II) with mp 258-260°C (from benzene). Compound II was identical to the substance obtained by the method in [1] with respect to its melting point and IR spectrum.

N-Methylpyrrolanthrone (III). A) 0.5-g sample of acid VIII was heated in 25 ml of 85-88% phosphoric acid at 120-130°C for 1 h. The product was isolated and purified by the methods used in the preparation of II.

B) A 0.5-g (1.65 mmole) sample of azide XIV was added to a solution of 1 g (14.5 mmole) of sodium nitrite in 25 ml of acetic acid and 25 ml of water, and the mixture was stirred at room temperature for 6 h. It was then diluted with 100 ml of water, and the resulting precipitate was removed by filtration, dried, and chromatographed on SiO_2 (100-250 mμ) (elution with benzene) to give 0.13 g (32%) of III.

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AUTOXIDATIVE TRANSFORMATIONS OF 2-SUBSTITUTED 3-ALKYL-4-HYDROXY-1-OXO-1,2-DIHYDROISOQUINOLINES

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UDC 547.833.7:542.943

A method for the preparation of 2-substituted 3-alkyl-4-hydroxy-1-oxo-1,2-dihydroisoquinolines is described. It is shown that 2,3-dialkyl-substituted derivatives readily undergo autoxidation and dealkylation to give N-methylphthalonimide and 3-hydroperoxy- and 3-hydroxy-2,3-dialkyl-1,4-dioxo-1,2,3,4-tetrahydroisoquinolines.

2,3-Dialkyl-5-1-oxo-hydroxy-1,2-dihydroisoquinolines are capable of facile oxidative transformations, whereas their 3-aryl analogs are resistant to autoxidation by air oxygen [1].

It is known [2, 3] that compounds with a double bond in the β position relative to the nitrogen atom in many cases are capable of oxidation. 3-Hydroperoxypyrrolenines and other

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