4. Ya. P. Stradyn', V. P. Kadysh, and S. A. Giller, Khim. Geterotsikl. Soedin., No. 12, 1587 (1973).
5. P. Zuman and I. M. Kolthoff (editors), Progress in Polarography, Vol. 2, New York–London (1962), p. 487.
6. R. A. Gavar, Yu. A. Bender, L. Kh. Baumane, and Ya. P. Stradyn', Zh. Obshch. Khim., 43, 1584 (1973).
7. Ya. Stradyn', I. Tutane, O. Neiland, and G. Vanag, Dokl. Akad. Nauk SSSR, 166, 631 (1966).
8. Ya. P. Stradyn' and V. P. Kadysh, Coll. Czech. Chem. Commun., 36, 698 (1971).
9. I. K. Tutane and Ya. P. Stradyn', Élektrokhimiya, 4, 398 (1968).
10. Ya. P. Stradyn', I. Ya. Kravis, and A. K. Grinvalde, Summaries of Papers Presented at the Fourth All-Union Conference on the Chemistry of Dicarbonyl Compounds [in Russian], Riga (1976), p. 158.
11. H. O. House, E. Feng, and N. P. Peet, J. Org. Chem., 36, 2371 (1971).

HETERORING CONTRACTION IN 1-DIAZOANTHRAPYRIDONE*

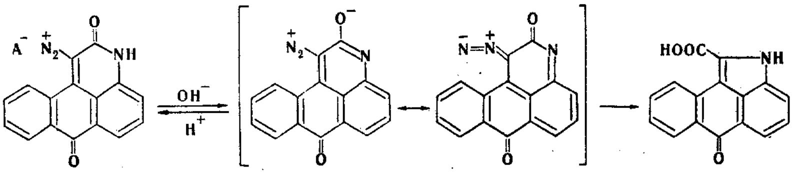
M. V. Kazankov, N. P. Makshanova,
and E. G. Kuznetsova

UDC 547.75:542.952

Anthrapyridone-1-diazonium salts are converted with ring contraction to pyrroloanthrone-1-carboxylic acid and, in the presence of alcohols, to its esters.

Pyrroloanthrone (6H-naphth[1,2,3-cd]indol-6-one) and its derivatives are difficult to obtain, and little study has been devoted to them. We have found a new method for the preparation of this heterocyclic polycondensed system – contraction of the ring in anthrapyridone-1-diazonium salts (1-diazo-7H-dibenz[f,ij]isoquinoline-2,7[3H]-dione) (I) to give pyrroloanthrone-1-carboxylic acid (II). Since, as shown in [2], the starting 1-aminoanthrapyridine and its substituted derivatives are extremely accessible, this method may have preparative value.

Salts I, which we obtained for the first time in the form of the hydrosulfates, tetrafluoroborates, and perchlorates, are stable crystalline substances. They undergo conversion to acid II even when they are dissolved in water, and the reaction is accelerated by the addition of alkalis, heating, and irradiation with daylight or UV light. The reaction proceeds instantaneously in strongly alkaline media, but small amounts of impurities (primarily 1-hydroxyanthrapyridone) are observed in this case. To reduce the amount of impurities and achieve high yields of acid II, it is expedient to carry out the reaction under the influence of weaker alkaline agents (for example, alkali-metal acetates or carbonates) and in mixtures of water and organic solvents. Derivatives of acid II that contain substituents in the anthrone fragment can also be obtained under the same conditions, as shown in the case of the synthesis of 3-methyl-5-bromopyrroloanthrone-1-carboxylic acid (III) (Table 1).



I VII II

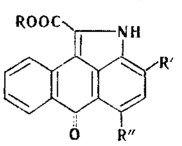
The structure of product II was proved by decarboxylation to pyrroloanthrone IV and subsequent arylation with bromobenzene to give N-phenylpyrroloanthrone V, which was identical to the substance synthesized by an independent method by cyclization of N-(1-anthraquinonyl)-N-phenylglycine VI [3].

---

* See [1] for our preliminary communication.

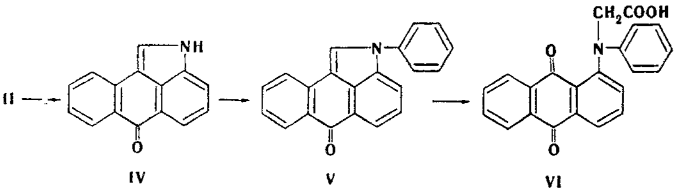
Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1103-1105, August, 1977. Original article submitted November 17, 1975.

TABLE 1. Pyrroloanthrone-1-carboxylic Acids and Their Methyl Esters



Compound	R	R′	R″	mp, °C (crystallization solvent)	Found, %				Empirical formula	Calc., %				Yield, %
					C	H	Hlg	N		C	H	Hlg	N	
II	H	H	H	—* (aqueous acetone)	73,0	3,6	—	5,6	$C_{16}H_9NO_3$	73,0	3,5	—	5,3	92
III	H	CH_3	Br	—* (aqueous dioxane)	57,3	2,5	22,8 (Br)	3,9	$C_{17}H_{10}BrNO_3$	57,3	2,7	22,5 (Br)	4,0	90
VIII	CH_3	H	H	246—247,5 (benzene)	73,8	4,3	—	5,1	$C_{17}H_{11}NO_3$	73,6	4,0	—	5,0	80
IX	CH_3	CH_3	Br	Above 350 (benzene)	58,6	3,3	21,6 (Br)	3,9	$C_{18}H_{12}BrNO_3$	58,4	3,2	21,6 (Br)	3,8	63
X	CH_3	H	Cl	292—293 (benzene)	66,0	3,3	11,0 (Cl)	4,3	$C_{17}H_{10}ClNO_3$	65,6	3,2	11,4 (Cl)	4,5	65

* Compounds II and III decompose above 300°C.



Ring contraction is characteristic for various diazo compounds that are capable of undergoing conversion to an o-quinone diazide form [4]. In our case the formation of an unstable intermediate, which evolves nitrogen to give acid II, can also be observed when the reaction is carried out in moderately alkaline (pH ~ 10) or close-to-neutral media. When a solution of diazonium sulfate I, which is red (λ_{max} 530 nm), is diluted or made alkaline with sodium acetate, a violet-blue substance (λ_{max} 580 nm) is formed (Fig. 1). The latter, in contrast, to diazonium salt I, passes from the aqueous layer to the organic solvents and on acidification is recoverted to starting salt I. The IR spectrum of a chloroform solution of the compound contains the band of a diazo group at 2190 cm^{-1}, which is shifted to the low-frequency side as compared with the $\nu_{N_{(2)}}$ band of diazonium salts I (2230 cm^{-1}). A comparison of the data obtained in this study with the known properties of quinone diazides [4] makes it possible to assign quinone diazide structure VII to this compound.

It is known that the rearrangement of diazo carbonyl compounds in the presence of alcohols or amines leads to the formation of, respectively, esters and amides of carboxylic acids [5]. Proceeding from this, we attempted to accomplish similar transformations for diazo compound I. We found that the action of amines

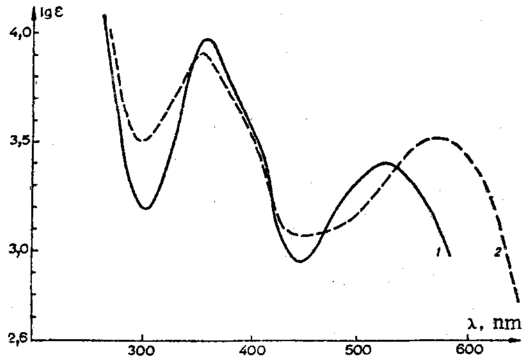


Fig. 1. Absorption spectra of anthrapyridone-1-diazonium hydrosulfate: 1) in water; 2) in a buffer solution at pH 9.8.

does not give amides of acid II but leads to the formation of 1-aminoanthrapyridone; this is evidently associated with the intermediate formation of diazoamino compounds. At the same time, esters of acid II are formed in the presence of alcohols. Thus methyl esters VIII-X (Table 1) were obtained by treatment of diazonium salt I and its derivatives with sodium carbonate in methanol—dioxane. The methyl esters, in contrast to the acids themselves, are quite soluble in organic solvents, and this makes them more convenient starting compounds for subsequent transformations.

EXPERIMENTAL

The absorption spectra of the compounds were recorded with a Perkin–Elmer 402 spectrophotometer.

Anthrapyridone-1-diazonium Hydrosulfate (I). A total of 8 ml (8 mmole) of a 1 N solution of nitrosylsulfuric acid was added to a suspension of 2 g (7.64 mmole) of 1-aminoanthrapyridone in 50 ml of glacial acetic acid, and the mixture was stirred for 2 h. The resulting red crystals were removed by filtration, washed with ether, and dried in a vacuum desiccator to give 2 g (70%) of salt I with mp 183-185°C (dec.). Found: C 51.4; H 2.3; N 10.9; S 8.6%. $C_{16}H_9N_3O_3S$. Calculated: C 51.7; H 2.4; N 11.3; S 8.6%.

4-Methyl-6-bromoanthrapyridone-1-diazonium and 6-chloroanthrapyridone-1-diazonium hydrosulfates were similarly obtained.

Pyrroloanthrone-1-carboxylic Acids (II, III). The appropriate anthrapyridone-1-diazonium hydrosulfate [25 g (55.7-70.5 mmole)] was added to a mixture of 500 ml of dioxane, 100 ml of water, and 25 g (236 mmole) of sodium carbonate, and the mixture was heated to 45°C for 30 min. It was then poured into 2.5 liters of water, and the resulting precipitate was removed by filtration, washed, and dried to give acids II or III (Table 1).

Methyl Pyrroloanthrone-1-carboxylates (VIII-X). A 25-g (55.7-70.5 mmole) sample of the appropriate diazo compound was added to a mixture of 500 ml of dioxane, 100 ml of methanol, and 25 g (236 mmole) of anhydrous sodium carbonate, and the mixture was heated to 70°C for 20 min. It was then diluted with 2.5 liters of water, and the resulting precipitate was removed by filtration, washed, dried, and chromatographed on Al_2O_3 (elution with chloroform) to give esters VIII-X (Table 1).

Pyrroloanthrone (IV). This compound was obtained by decarboxylation of acid II in a vacuum sublimator at 300-310°C (10 mm). Chromatographic purification on Al_2O_3 (elution with chloroform) gave the product, with mp 258-260°C (from benzene) (mp 250-251°C [6]), in 48% yield.

N-Phenylpyrroloanthrone (V). A mixture of 0.9 g (4 mmole) of pyrroloanthrone IV, 3.5 ml (30 mmole) of bromobenzene, 0.35 g (1 mmole) of cuprous bromide, and 70 ml of nitrobenzene was refluxed for 16 h, after which it was cooled and filtered. The nitrobenzene was removed from the filtrate by steam distillation, and the solid was removed by filtration, dried, and subjected to chromatographic purification on Al_2O_3 (elution with chloroform) to give 0.6 g (51%) of anthrone V with mp 226°C (from alcohol). Compound V was identical with respect to its melting point and IR spectrum to the compound obtained by the method in [3].

LITERATURE CITED

1. M. V. Kazankov and N. P. Makshanova, Zh. Vses. Khim. O-va, 19, 461 (1974).
2. M. V. Kazankov, G. I. Putsa, and L. L. Mukhina, Khim. Geterotsikl. Soedin., No. 12, 1651 (1972).
3. German Patent No. 270789 (1914); Frdl., 11, 574 (1915).
4. L. A. Kazitsina, V. S. Kikot', and A. V. Upadysheva, Usp. Khim., 35, 881 (1966).
5. L. L. Rodina and I. K. Korobitsina, Usp. Khim., 36, 611 (1967).
6. German Patent No. 594168 (1934); Frdl., 19, 1962 (1934).