# OXIDATION OF 4-STYRYL-2-PHENYL-5,6-BENZOQUINOLINE WITH POTASSIUM PERMANGANATE

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UDC 547.832.5'313:542.943

Oxidation of 4-styryl-2-phenyl-5,6-benzoquinoline with potassium permanganate gave phenyl 2-phenyl-5,6-benzo-4-quinolyl diketone, 2-phenyl-4-formyl-5,6-benzoquinoline, 2-phenyl-5,6-benzocinchoninic acid, and benzoic acid. It is shown that phenyl 2-phenyl-5,6-benzo-4-quinolyl diketone is cleaved under the influence of $OH^-$ ions to the corresponding aldehydes and carboxylic acids; this is explained by the decisive effect of the acidity of the media on the direction of the reaction.

The oxidation of quinoline and 6,7-benzoquinoline derivatives to carboxylic acids by means of potassium permanganate is discussed in a number of papers (for example, see [1, 2]). There is no information in the literature regarding other products of the oxidation of such compounds.

We have found that the pH of the medium has a decisive effect upon the direction of the oxidation of 4-styryl-2-phenyl-5,6-benzoquinoline (I) under the conditions of the Wagner reaction. In acetic anhydride, which is a buffer (pH 7) in this reaction, the predominant oxidation product is phenyl 2-phenyl-5,6-benzo-4-quinolyl diketone (III). The ratio of oxidation products changes in weakly alkaline media (pH 8), and 2-phenyl-4-formyl-5,6-benzoquinoline (IV), 2-phenyl-5,6-benzocinchoninic acid (V), and benzoic acid (VI) constitute a considerable fraction. The oxidation products in alkaline media (pH 9-12) are IV-VI and 2-phenyl-5,6-benzoquinoline (VII), which is probably formed by partial decarboxylation of acid V (Table 1).

It is natural to assume that hydrolytic cleavage of the unsymmetrical $\alpha$-diketone formed in the reaction occurs as $OH^-$ ions accumulate.

The relatively low electron density in the 4-position of the heteroring should favor reaction via path A, while the presence of steric hindrance on the part of the 5,6-benzoquinoline ring directs the reaction via path B.

The experimental data confirm the above assumption. At pH 13, after 1 h at 70°C, $\alpha$-diketone III is cleaved (42%) via path A in the scheme following and via path B (58%), which attests to the predominant effect of steric factors on the cleavage.

TABLE 1. Dependence of the Yields of Reaction Products on the Oxidation Conditions

| Expt. No. | Oxidation conditions | | | | Yield of reaction products based on the amount of I used in the reaction, % | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | solvent | pH at end of expt. | $t$, °C | time, h | I | III | IV | V | VI | VII |
| 1 | Aqueous dioxane (80%) | 12 | 50—60 | 3 | 88 | — | 5 | 3 | — | — |
| 2 | " " " | 12 | 100 | 1 | 30 | — | 14 | 28 | 11 | 7 |
| 3 | " " " | 8 | 100 | 1 | 25 | 28 | 11 | 22 | 10 | — |
| 4 | " " " | 9,5 | 100 | 4 | 25 | — | 10 | 20 | 14 | 22 |
| 5 | Aqueous pyridine (85%) | 8 | 5 | 5 | — | 20 | 28 | 36 | 11 | — |
| 6 | " " " | 9 | 5 | 5 | 11 | — | 19 | 55 | 10 | — |
| 7 | Acetic anhydride–toluene (1.5:1) | 7 | 5 | 3 | — | 54 | — | 19 | 10 | — |

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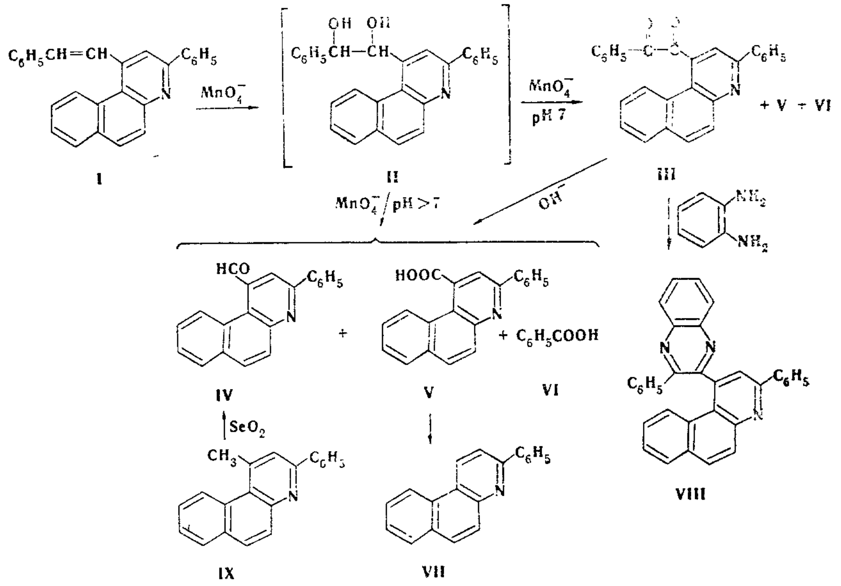
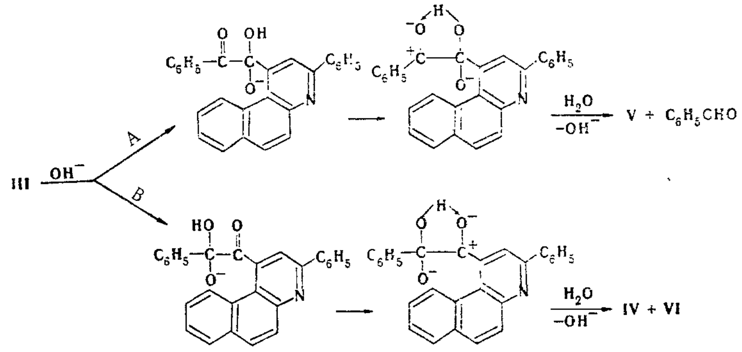
Institute of Physical Organic Chemistry, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1121-1124, August, 1974. Original article submitted May 30, 1973.



According to [3, 4], the production of α-diketones under the conditions of the Wagner reaction is observed only in exceptional cases. This fact probably should be explained by the sensitivity of compounds of this sort to changes in the acidity of the medium.

We have found that the solvent and reaction temperature affect the rate of oxidation. Thus, only a very small amount of oxidation occurs in dioxane at 50-60° – up to 90% of the starting benzoquinoline is recovered after 3 h, and only traces of the oxidation products (Table 1) are formed. In refluxing dioxane, 70% oxidation is observed after 1 h. The use of pyridine or acetic anhydride as the solvent makes it possible to lower the temperature to 5°.

Thus, we have isolated all of the possible oxidation products, except α-glycol II, in the oxidation of benzoquinoline I with potassium permanganate and have determined the conditions for their directed synthesis. We were unable to carry out the oxidation under hydroxylation conditions because of the high hydrophobic character of the starting compound. This reaction may prove to be a convenient method for the synthesis of α-diketones from styryl derivatives of nitrogen-containing heterocycles.



The structures of the compounds that we obtained in this research were proved by IR and UV spectroscopy and by chemical transformations. Thus, the K band (315-330 nm) due to the exocyclic double bond of the styryl group vanishes in the electronic spectra of the oxidation products, and the UV spectra take on the form characteristic for 5,6-benzoquinolines [5].

## EXPERIMENTAL

The individuality of the compounds obtained was verified by thin-layer chromatography (TLC) on a loose layer of activity II aluminum oxide in a benzene–cyclohexane (2 : 1) system with development by iodine vapors. The pH values were measured with a pH-262 laboratory pH meter. The UV spectra of ethanol solutions were recorded with a Specord UV-vis spectrophotometer. The IR spectra of KBr pellets were recorded with a UR-20 spectrometer.

Oxidation of 4-Styryl-2-phenyl-5,6-benzoquinoline (I). (General Method). A 4.8-g (30 mmole) sample of finely ground potassium permanganate (in experiments 1, 2, and 6, 3 g of

KOH was also added) was added in portions to a solution of 3.6 g (10 mmole) of benzoquinoline I [5] in an appropriate solvent. At the end of the experiment, the mixture was worked up by one of the methods indicated below, depending on the solvent. The solvent, the pH of the medium, the reaction time and temperature, and the yields of reaction products are presented in Table 1.

A. Oxidation in Pyridine or Dioxane. The dark-brown precipitate was removed by filtration and washed with solvent and hot water. The filtrate was concentrated to 50 ml, and the neutral reaction products were extracted with benzene. The extract was dried with $MgSO_4$, the solvent was removed, and the dry residue was chromatographed with a column filled with $Al_2O_3$ [by elution with benzene–cyclohexane (2 : 1)]. This procedure yielded unchanged benzoquinoline I [mp 173°, $R_f$ 0.86 (benzene)], phenyl 2-phenyl-5,6-benzo-4-quinolyl diketone (III) [bright-yellow needles with mp 200-201° (from benzene) and $R_f$ 0.59 (benzene); IR spectrum: 1670 and 1685 $cm^{-1}$ (CO). Found: C 83.5; H 4.6; N 3.6%. $C_{27}H_{17}NO_2$. Calculated: C 83.7; H 4.4; N 3.6%] and 2-phenyl-4-formyl-5,6-benzoquinoline (IV) [mp 130-131° (from aqueous dioxane), $R_f$ 0.77 (benzene). The 2,4-dinitrophenylhydrazone had mp 289-290° (from dioxane). At pH 9.5-10, the color of an aqueous dioxane solution changed from bright-yellow to red. Found: N 14.9%. $C_{26}H_{17}N_5O_4$. Calculated: N 15.1%. According to [6], aldehyde IV has mp 131° (from aqueous dioxane), and its 2,4-dinitrophenylhydrazone has mp 249° (from dioxane). Aldehyde IV was chromatographically and spectroscopically identical to the compound obtained from benzoquinoline IX by the method in [6]]. The aqueous layer was acidified to pH 2, and the precipitated 2-phenyl-5,6-benzocinchoninic acid (V), with mp 296-297° (from acetic acid) [7], was removed by filtration. Benzoic acid (VI), with mp 121-122° (from water), was extracted from the filtrate with ether.

B. Oxidation in Acetic Anhydride. Ethyl acetate (50-70 ml) and 60 ml of 15% aqueous sodium bisulfite solution were added to the reaction mixture, and it was cooled and stirred until it became colorless. The organic layer was washed repeatedly with water and alkali and concentrated to 30 ml. The concentrate was dissolved in pyridine–ethyl acetate (1 : 1) and decomposed in the cold with 30 ml of water. The precipitated diketone (III) was removed by filtration. The organic layer was washed with alkali, acid, and water and dried. Evaporation of the solvent gave an additional amount of diketone III. Acids V and VI were isolated from the aqueous layer as described in method A.

2,4-Dinitrophenylhydrazone of Diketone III. A total of 10 ml of a solution of 2,4-dinitrophenylhydrazine in phosphoric acid and ethanol [8] was added to a solution of 0.39 g (1 mmole) of diketone III in alcohol–dioxane (2 : 1), and the mixture was heated on a boiling-water bath for 3 h. The hydrazone was precipitated by the addition of ether to give 0.35 g (63%) of yellow needles. IR spectrum: 1335, 1500 ($NO_2$); 1610-1620 (C=N); 1680 (C=O); 3280 (N–H) $cm^{-1}$. A change in the color of an aqueous dioxane solution of the hydrazone from bright-yellow to ruby red was observed at pH 8.7-9.0. Found: C 70.0; H 3.8; N 12.3%. $C_{33}H_{21}N_5O_5$. Calculated: C 69.9; H 3.7; N 12.3%.

2-Phenyl-4-(2-phenyl-3-quinoxalyl)-5,6-benzoquinoline (VIII). A solution of 0.5 g (1.3 mmole) of diketone III and 0.15 g (1.5 mmole) of o-phenylenediamine in acetic acid was heated at 125° for 2 h, after which it was cooled and poured over ice. The precipitated benzoquinoline (VIII) was washed with water and dried to give 0.5 g (90%) of large cubical light-beige crystals with mp 204-205° (from dimethylformamide–alcohol). Found: C 86.1; H 4.7; N 9.1%. $C_{33}H_{21}N_3$. Calculated: C 86.3; H 4.6; N 9.1%.

Hydrolytic Cleavage of α-Diketone III. Aqueous alkali was added to a solution of 1g (2.5 mmole) of diketone III in 150 ml of alcohol–dioxane up to pH 13, and the mixture was stirred and refluxed for 1h. The solvent was then evaporated under normal conditions, during which the benzaldehyde was oxidized to acid VI. The dry residue was treated with water and benzene, and the cleavage products were separated by method A to give 0.31 g (40%) of aldehyde IV, 0.18 g (22%) of acid V, 0.22 g (70%) of acid VI, and 0.043 g (6%) of benzoquinoline VII [(mp 188-189° (from toluene) [5, 7]].

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