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# Synthesis and Photochromism of Pyrazoleanthrones and Fyrazolenaphtacencnes

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# SYNTHESIS AND PHOTOCHROMISM OF PYRAZOLEANTHRONES AND PYRAZOLENAPHTACENONES

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Abstract Photoactive 5- and 7-phenoxysubstituted of pyrazolanthrones and 8-phenoxysubstituted of pyrazolenaphtacenones, its N-butyl-, N-acetylderivatives are synthesizied.

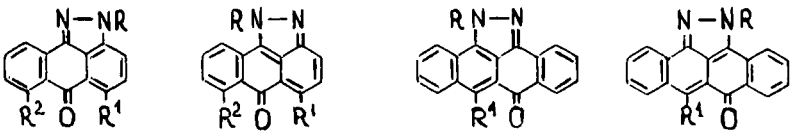
## INTRODUCTION

Peri-aryloxysubstituted para-quinones (anthraquinone, naphtacenonequinone) are reversibly isomerizates to peri-aryloxysubstituted ana-quinones under action of light of different spectral composition[1]. This phenomenon was further investigated by example of heterocyclic derivatives of anthrone and naphtacenone. It was found that para-methylenequinoid structure of these compounds undergoes the rearrangement into ana-methylenquinoid one under action of light i.e. they are also photochromic[2]. In order to investigate the spread region of this type photochromism the following compounds with quinoneimine structure - peri-phenoxyderivatives of pyrazolanthrone and pyrazolenaphtacenone were synthesizied.

## Synthesis

Pyrazolanthrones are obtained with method[3] by interaction of 1,4- and 1,5-dichloro- and diphenoxyanthraquinones with hydrazinehydrate in pyridine. The first representatives of heterocyclic combination new class - pyrazolenaphtacenones have been synthezed by the analogous method. Acetylderivatives of pyrazolanthrones and pyrazolenaphta-

cenones are synthesized by short-time heating of pyrazolanthrones, pyrazolenaphtacenones in acetic anhydride. At treatment of pyrazolanthrones and pyrazolenaphtacenones with butyl iodide in dimethylformamide in presence of potash by the method[4] the butylderivatives are formed. Corresponding compounds - 1-butylpyrazolanthrones and 2-butylpyrazolenaphtacenones were isolated from reaction mass with yield of 15% and 30%.



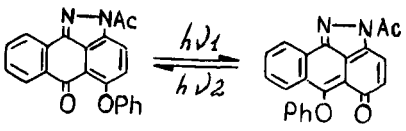
R= H, Ac, Bu; $R^1$, $R^2$= H,Cl,OPh

Photochemical properties

Photochemical activity off all synthesized compounds was cheked. EAS of toluene solution of compounds prepared in darkness were recorded and then after exposition of these solutions in UV- and short-wave visible light.

Pyrazolanthrones with chlorine atom in 5- and 7-position and pyrazolenaphtacenones with clorine atom in 8-position including N-acetyl- and N-butylderivatives are photostable. Pyrazolanthrones and pyrazolenaphtacenones with phenoxyl group in 5-, 7- and 8-position are photoactive.

Under expositions of 5-phenoxypyrazolanthrone toluene solution in UV- and short-wave visible light there is appeared a low intensive absorption band on dip of the main absorption band which is not disappeared at the following radiation with long-wave visible light. Photochemical behavior of 5-phenoxypyrazolanthrone is difficult to interpret uniquely because the course of photoinduced prototropy is possible here. The 2-acetyl-5-phenoxypyrazolanthrone conducts itself as typical photochrome compound (fig.1). The reversibility and the specific features of the obser-



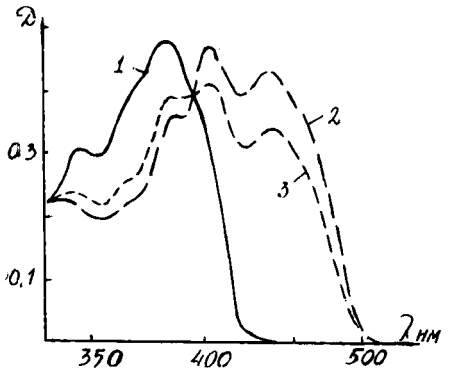
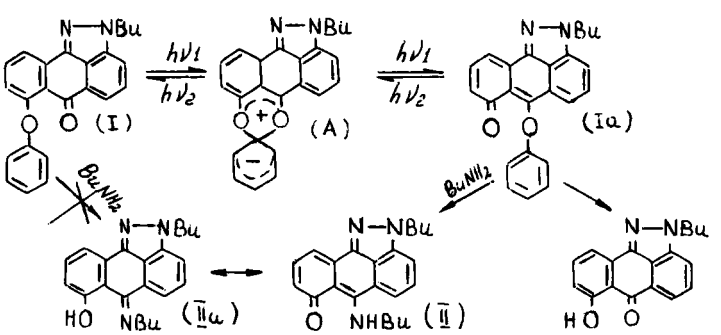



FIGURE 1 EAS of toluene solution of 2-acetyl-5-phenoxypyrazolanthrone prepared in darkness (1), after exposition of these solution in UV-(2), and short-wave visible (3) light.

ved spectral changes suggest that the photocromism of 2-acetyl-5-phenoxypyrazolanthrone is also a result of the photoinduced arylotropic rearrangement[1].

The 7-phenoxypyrazolanthrones have photochromic properties but photochromism of these compounds is complicated with destruction of photoinduced up to corresponding 7-hydroxyderivatives.

Attention is drawn to the fact that long-wave absorption band of 2-butyl-7-phenoxypyrazolanthrone appeared after radiation of toluene solution is batochromically shifted even in comparison with the most long-wave absorption band of butylaminopyrazolanthrone (II) in ethanol. It is known that photoarylothropy of aryloxy-p-quinones is described



as intramolecular nucleophilic substitution proceeding through intermediate $\sigma$-complex[1]. Probably, it is possible to suppose that long-wave absorption of radiated toluene solution of 7-phenoxypyrazolanthrones belong to $\sigma$-complex (A) stabilized with annelated to anthrone ring $\pi$-excessive pyrazole cycle.

Spectral alterations observed by radiation of toluene solution 8-phenoxypyrazolenaphtacenone can probably be conneted as well as in case of 5-phenoxypyrazolanthrone the phenomenon of photoinduced prototropy.

The 1-acetyl-8-phenoxypyrazolenaphtacenone as well as 2-acetyl-5-phenoxypyrazolanthrone possed the typical photochromic combination properties.

## Conclusions

Photochromic peri-phenoxyderivatives of pyrazolanthrone and pyrazolenaphtacenone are synthesized.

By example of 7-phenoxypyrazolanthrone it is spectrally fixed the formation of $\sigma$-complex formed during photoarylotropic rearrangement of para-quinoneimine structure in ana-quinoneimine one.

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