

[a027]

New product of pyromellitic anhydride condensation with 1,2-phenylenediamine.

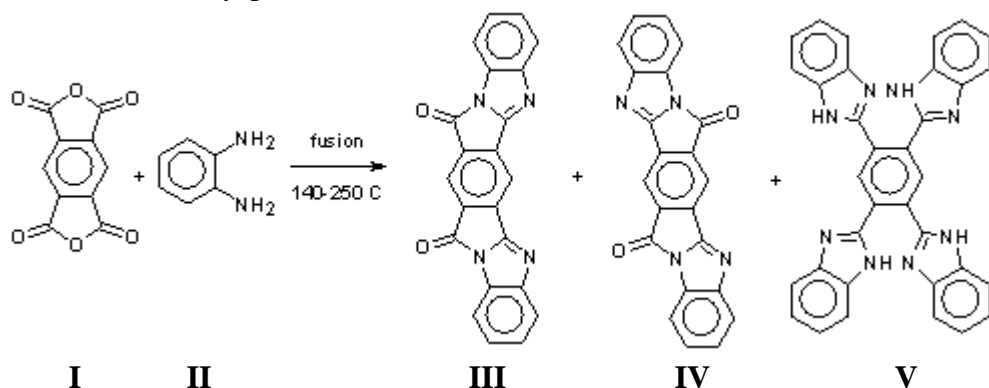
Vladimir N. Bulavka

Scientific-Research Phototechnical Institute - Slavich, Ltd., Mendeleev sq. 2, bldg. 39-a, Pereslavl-Zalesskiy, Yaroslavl region, 152020, Russian Federation. E-mail: v.bulavka@mail.ru

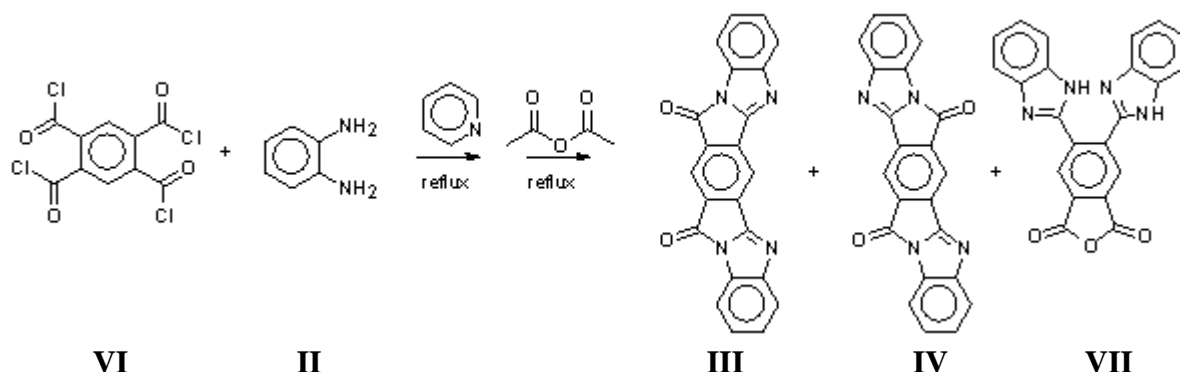
Keywords: Pyromellitic anhydride, 1,2-phenylenediamine, bisbenzimidazole pigment.

Abstract. During study of pyromellitic anhydride condensation with 1,2-phenylenediamine to bisbenzimidazole pigment new condensation product, di-2,3-(2-benzimidazolyl)-benz[4,5]imidazo[2,1-a]isoindol-11-one was obtained.

Fusion of pyromellitic anhydride (**I**) with 1,2-phenylenediamine (**II**) gives bisbenzimidazole pigments mixture of cis-configuration (**III**) and trans-configuration (**IV**) as main product. 1,2,4,5-Tetra(2-benzimidazolyl)benzene (**V**) was detected as by-product [1].

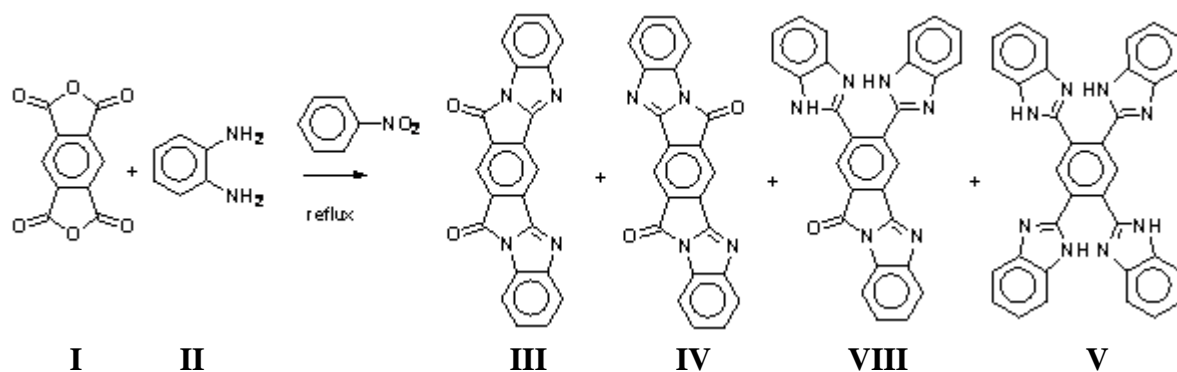


Reaction of pyromellitic tetrachloroanhydride (**VI**) with **II** in pyridine with subsequent action of acetic anhydride also gives **III** and **IV** as main product. In this reaction 5,6-di(2-benzimidazolyl)phthalic anhydride (**VII**) was isolated as by-product [2].

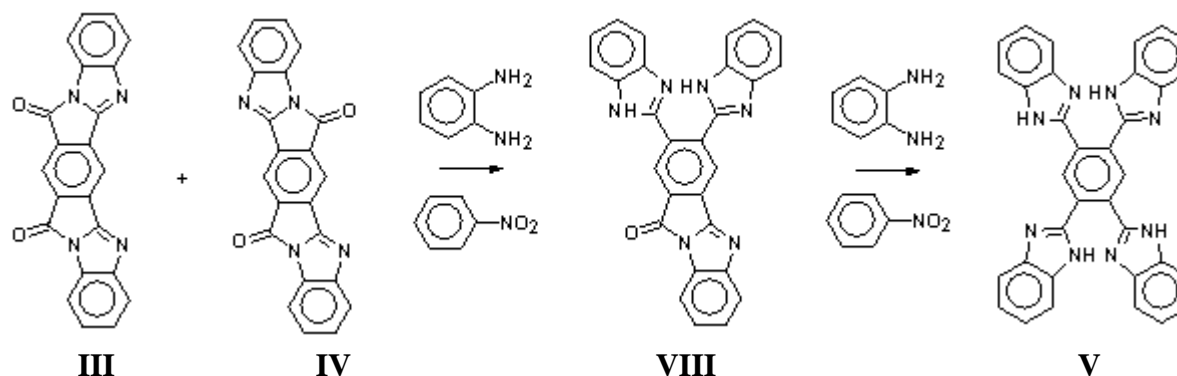


The pigments type **III** and **IV** mixture earlier also were obtained in boiling nitroarene solvents, generally, with low yields [3].

We have conducted more detailed study of **I** and **II** condensation in refluxing nitrobenzene as solvent. The course of condensation was similar to fusion, and desired mixture of **III** and **IV** was readily separated by precipitation. However, in mother liquor not only **V**, but significant quantity of new compound was detected. When excess of starting **II** was 50-70% above new compound prevailed as reaction product. On basis of MS and NMR spectra for this new compound di-2,3-(2-benzimidazolyl)-benz[4,5]imidazo[2,1-a]isoindol-11-one structure **VIII** was determined.



Formation of compounds type **V** from compounds type **III** and **IV** earlier was studied for oligomeric and polymeric substrates [4]. Based on above results we propose a mechanism of formation **VIII** from **III** and **IV** mixture by nucleophilic attack of **II** as intermediate of final **V** formation by double nucleophilic attack of **II** on **III** and **IV** mixture.



We have elaborated optimal conditions for obtaining **VIII** as main product of reaction.

Experimental.

Di-2,3-(2-benzimidazolyl)-benz[4,5]imidazo[2,1-a]isoindol-11-one (VIII). To the boiling solution of **I** (0.1 mol) in nitrobenzene solution of **II** (0.32 mol) in nitrobenzene was added and heated at reflux 3 hr. After cooling precipitate (**III** and **IV**) was formed. Precipitate was filtered and washed with nitrobenzene. The filtrate was evaporated under reduced pressure and the residue was subjected to column chromatography on silica gel in 1,2-dichloroethane – nitrobenzene as eluent. Subsequently, **V** ($M = 542$), **VIII** ($M = 452$) [5], **III** ($M = 362$), and **IV** ($M = 362$) were eluted. The yield of **VIII** was 60-65%.

References.

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5. MS m/z (%): $M+1 = 453$ (31), $M = 452$ (100), 451(77), 424(7), 423(7), 363(15), 362(80), 336(6), 334(5), 333(5), 306(5), 305(12), 226(5), 216(5). $^1\text{H NMR}$ (CD_3SOCD_3), ppm: 7.35-7.55 (m., 4H), 7.70-7.90 (m., 4H), 8.49 (s., 1H) 8.51 (s., 1H).