

[A0036]

Hydrazinolysis of 1,2,4,5-benzenetetracarboxylic bis-(substituted)phenylimides.

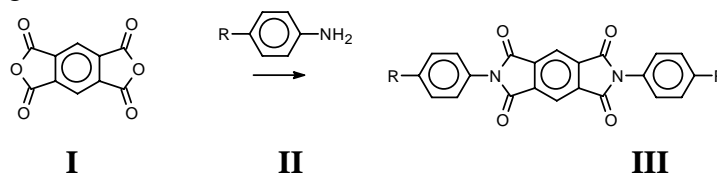
Vladimir N. Bulavka, Vasilii F. Aristov

Research Institute of Cosmic and Aviation Materials Co., Ltd., Mendeleev sq. 2, bldg. 31,
 Pereslavl-Zalesskiy, Yaroslavl region, 152020, Russian Federation. E-mail:
v.bulavka@mail.ru, v-bulavka@niikam.ru

Keywords: Pyromellitic anhydride, 1,2,4,5-benzenetetracarboxylic dianhydride, pyromellitic acid bis(substituted)phenylimide, 1,2,4,5-benzenetetracarboxylic bis(substituted)phenylimide, hydrazinolysis, 2,3,7,8-tetrahydropyridazino[4,5-g]phthalazin-1,4,6,9-tetrone.

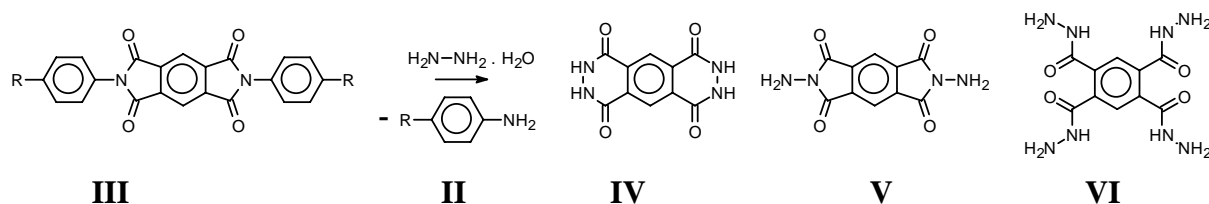
Abstract. Hydrazinolysis of pyromellitic acid bis-(substituted)phenylimides with hydrazine hydrate in high-boiling alcohols as solvents leads to 2,3,7,8-tetrahydropyridazino[4,5-g]phthalazin-1,4,6,9-tetrone as sole product.

Reaction of pyromellitic anhydride (**I**) and (substituted) anilines (**II**) 1 : 2 mixture gives bis-(substituted)phenylimides (**III**) as reaction products [1, 2]. We have obtained above bis-imides **III** in boiling 2,4-dichlorotoluene as solvent.



R = H, CH₃, OCH₃, O(4'-C₆H₄NH₂).

Reaction of **III** hydrazinolysis theoretically can to proceed with formation of several reaction products derived from pyromellitic acid – cyclic hydrazide **IV**, its aminoimide isomer **V**, and tetrahydrazide **VI**. Other reaction product is (substituted) aniline 4-RC₆H₄NH₂.



Earlier it was shown that hydrazinolysis of polyimides and some model compounds proceeds with cyclic hydrazides formation as sole products [3].

We have carried out **III** hydrazinolysis with hydrazine hydrate in various alcoholic solvents: methylcellosolve, ethylcellosolve, ethylene glycol and have found that main reaction product is 2,3,7,8-tetrahydropyridazino[4,5-g]phthalazin-1,4,6,9-tetrone **IV** (was identified by comparison with reference compound), isolated from reaction mixture with 70-80% yield. Earlier **IV** was obtained from **I** and hydrazine [4, 5].

Experimental.

Pyromellitic acid bis-(substituted)phenylimides (III) (general method). To the boiling solution of **I** (0.218g, 1 mmol) in 100ml of 2,4-dichlorotoluene warm solution of **II** (2 mmol) in 20-25 ml of 2,4-dichlorotoluene was added dropwise and heated at reflux 5 hrs. Solvent was removed at rotatory evaporator with oil bath heating and residue (crude **III**) was

recrystallized from acetic anhydride. Precipitate was filtered, washed with ethyl acetate, and dried. The yield of **III** was 70-85%. [Synthesis of **III** (R = O(4'-C₆H₄NH₂)) see in preceding poster].

2,3,7,8-Tetrahydropyridazino[4,5-g]phthalazin-1,4,6,9-tetrone (IV). To the boiling solution of **III** (0.1mmol) in alcoholic solvent 0.2-0.4mmol of hydrazine hydrate in the same solvent was added and heated at reflux 10-12 hrs. Solvent was removed at rotatory evaporator with oil bath heating. Residual crude **IV** was suspended in 2-propanol, filtered, washed with 2-propanol, and dried. The yield of **IV** was 70-80%.

References.

1. Meyer, H.; Steiner, K. Derivatives of pyromellitic acid and isomeric benzene polycarboxylic imides. *Monatsh. Chem.* 1914, **35**, 391-406.
2. Mosher, W. A.; Chlystek, S. J. N,N'-bis(substituted phenyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides. *J. Heterocycl. Chem.* 1972, **9**(2), 319-324.
3. Dine-Hart, R. A.; Wright, W. W. Reaction of hydrazine hydrate with polyimides. *Chem. Ind. (London)*. 1967, (37), 1565-1566.
4. Seka, R.; Muller, R. H. Zur kenntnis der pyromellithsaure (benzodiketohydrinden- und benzodipyridazinderivate). *Monatsh. Chem.* 1931, **57**, 86-96.
5. Drew, H. D. K.; Pearman, F. H. Chemiluminescent organic compounds. IV. Amino and hydrazinocyclophthalhydrazides and their relative luminescent power. *J. Chem. Soc.* 1937, 586-592.