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Synthesis of *endo,exo*-1,2,3,4,11,11-Hexachlorotricyclo[6.2.1.05,10]-undec-2-en-7,8-dicarboxylic acid *N*-(2,4,6-Tribromophenyl)imide

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Abstract—A preparation method was developed for *endo,exo*-1,2,3,4,11,11-hexachlorotricyclo-[6.2.1.0^{5,10}]undec-2-ene-7,8-dicarboxylic acid *N*-tribromophenylimide by acylation of 2,4,6-tribromoaniline with this acid anhydride. The structure of imide obtained was proved by IR spectrum, TLC method, and by independent synthesis.

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Among the indispensable qualities of the modern polymer materials the low inflammability and self-extinguishing are known to be required [1, 2] that can be ensured by introducing various modifiers serving as fire-retardants. Nowadays widely spread fire-retardants are nitrogen and halogen containing compounds. An important representative among this type fire-retardants is 2,4,6-tribromoaniline and its derivatives [3].

No published data exist on the application of imides based on 2,4,6 tribromoaniline and on the possibility of its reaction with anhydrides of dicarboxylic acids save [4], where by melting tribromoaniline with maleic anhydride under very stringent conditions (10-fold excess of maleic anhydride, 210°C, catalyst $ZnCl_2$) has been prepared *N*-(2,4,6-tribromophenyl)maleimide in 20% yield.

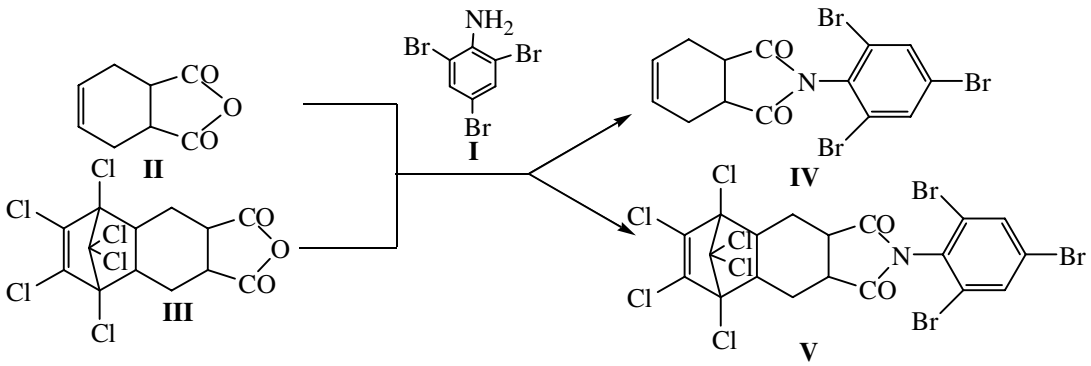
The low reactivity of tribromoaniline in acylation [5] is due to its low basicity and to steric hindrances from the *O*,*O*'-bromine atoms.

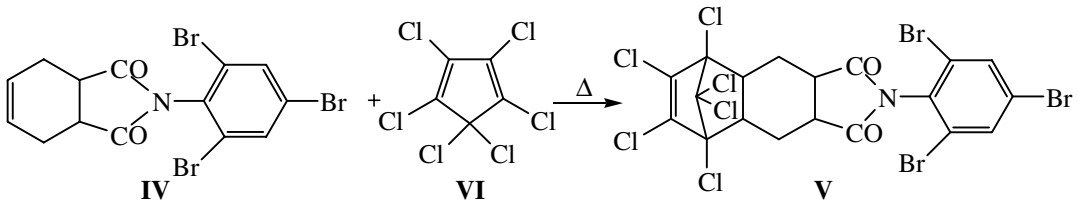
We developed synthesis conditions for *N*-(2,4,6-tribromophenyl)imides of cyclic dicarboxylic acids of tetrahydrophthalic and tricycloundecene series. Acylation of 2,4,6-tribromoaniline (**I**) with anhydrides of *cis*-4-cyclohexene-1,2-dicarboxylic acid (**II**) and *endo*,*exo*-1,2,3,4,11,11-hexachlorotricyclo[6.2.1.0^{5,10}]undec-2-ene-7,8-dicarboxylic acid (**III**) was performed at equimolar amounts of components, at 180±5°C for 36 h in sealed ampules [6, 7]. Compounds **IV** and **V** were obtained in high yields (~75%).

The increase in the temperature to 190°C at the reaction interval 25 h resulted in decrease in the yield of compounds **IV** and **V** to 65.9 and 60% respectively, and after 36 h the reaction products suffered tarring. At 170°C the yield of compounds **IV** and **V** also reduced to 53 and 50% respectively.

The structure of compounds **IV** and **V** was proved by IR spectroscopy. In the IR spectrum of compound **V** the absorption bands were observed in the region ν 1601, 1603 (C=O), 1778 and 1780 (C=C), 600–650 cm^{-1} (C–Br).

To prove the *endo*,*exo*-configuration and to develop a more efficient procedure for preparation of fire-retadant modifier we performed an independent synthesis of





IV **VI** **V**

compound **V**. A reaction of *cis*-*N*-2,4,6-tribromophenylimide (**IV**) with hexachlorocyclopentadiene (**VI**) at a molar ratio 2:1 and 140°C resulted within 2 h in 99% yield of *endo*,*exo*-*N*-(2,4,6-tribromophenyl)imide (**V**).

EXPERIMENTAL

IR spectra of compounds **IV** and **V** were recorded on a spectrophotometer UR-20 from mulls in mineral oil [8].

The purity of compounds was checked by TLC on Silufol plates using as eluent a mixture benzene–dichloroethane–acetic acid, 4:1.5:1 by volume, development under UV irradiation [9]. Molecular weight was measured by cryoscopy in camphor [10]. Initial high-purity 2,4,6-tribromoaniline was prepared by procedure we previously developed, a liquid-phase oxibromination of aniline [11].

Anhydrides of *endo*,*exo*-1,2,3,4,11,11-hexachlorotricyclo[6.2.1.$0^{5,10}$]undec-2-ene-7,8-dicarboxylic acid (**III**) and *cis*-4-cyclohexene-1,2-dicarboxylic acid (**II**) were prepared by procedures [12, 13] respectively.

***cis*-4-Cyclohexene-1,2-dicarboxylic acid *N*-(2,4,6-tribromophenyl)imide (IV).** Into an ampule was charged 10 g (0.066 mol) of 2,4,6-tribromoaniline and 22 g (0.06 mol) of anhydride **II**. The ampule was sealed and heated in a temperature-controlled device at 180°C for 36 h. Afterwards the ampule was cooled, opened, the reaction mixture was treated with ether to remove the unreacted 2,4,6-tribromoaniline. The precipitated crystals were filtered off and dried in air. Yield 20.9 g (75%), mp 168°C (from benzene), R_f 0.62. IR spectrum, ν, cm^{-1}: 1603 (C=O), 1780 (C=C), 600–650 (C–Br). Found, %: C 36.00; H 2.07; Br 51.2; N 3.0. *M* 462. $C_{14}H_{10}Br_3NO_2$. Calculated, %: C 36.00; H 2.17; Br 51.72; N 3.01. *M* 464.

***endo*,*exo*-1,2,3,4,11,11-Hexachlorotricyclo-[6.2.1.$0^{5,10}$]undec-2-ene-7,8-dicarboxylic acid *N*-(2,4,6-tribromophenyl)imide (V).** *a*. Into an ampule was charged 0.1 mol of compound **IV** and 0.2 mol of hexachlorocyclopentadiene (**VI**), and the mixture was heated for 12 h on an oil bath for 140°C. Then the content of the ampule was treated with hot pentane, the precipitated crystals were filtered off. Yield 14.51 g (99.8%), mp 298°C, R_f 0.74. Found *M* 735. Calculated *M* 737.

b. In 100 ml of DMF was dissolved 0.1 mol of *N*-2,4,6-tribromoaniline (**I**) and 0.1 mol of compound **III**, and the mixture was heated at reflux for 6 h. Then the mixture was poured at stirring into ice water, the precipitated crystals were filtered off, dried, and recrystallized from hot pentane. Yield 99.9%, mp 298°C. IR spectrum, ν, cm^{-1}: 1601 (C=C), 1778 (C=O), 600–650 (C–Br). Found, %: C 30.1; H 1.41; N 2.03; Hlg 63.80. $C_{19}H_{10}Cl_6Br_3NO_2$. Calculated, %: C 30.90; H 1.40; N 1.98; Hlg 64.46.

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