

## A New Method for the Synthesis of Bromine-Containing Heterocyclic Compounds for Photovoltaic Polymers

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### Abstract

With the development and improvement of systems for converting sunlight into electric and thermal energy, more and more work is emerging on the development of the newest and most promising direction in solar energy, namely the creation of solar cells based on photosensitive polymers. Recently the power conversion efficiency of organic photovoltaic (OPV) devices has overcome the barrier of 17%, and thus we can expect a new wave of scientific interest in the development of new, more efficient OPV devices. Unfortunately, during searching for highly efficient chemical structures of OPV polymers, the researchers missed an important point: all photovoltaic polymers consist of aromatic and heteroaromatic «building blocks», which, in turn, are synthesized based on outdated techniques using highly toxic, dangerous for life and environment precursors. The development of «green», environmentally friendly, economically viable methods for the synthesis of photovoltaic polymers and building blocks for their production, will make the energy obtained from OPV truly «green». In this work, we present an alternative, «green» method for synthesizing halogen-containing aromatic and heteroaromatic, expensive building blocks most commonly used in the synthesis of photovoltaic polymers, which can be used to obtain photovoltaic polymers of various structures. We present the original methods for the synthesis of 4,4-dibromo-1,1-biphenyl (1), 4,7-dibromo-2,1,3-benzothiadiazole (2), 2-bromothiophene (3) and 2,5-dibromothiophene (4). All these methods differ from the previously described routes by their simplicity and convenience of their implementation, the absence of corrosive and irritant reagents, good yield and compliance with the principles of «Green Chemistry».

### 1. Introduction

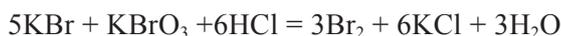
The main aim of development Photovoltaic polymers – is the creation of environmentally friendly methods of obtaining energy [1]. The urgency of the development of solar energy is not in doubt, but the future of Photovoltaic polymers based on solar cells caused some concerns because of their low efficiency compared to more efficient counterparts [2, 3]. For a long time, Photovoltaic polymers could not exceed the efficiency level of 10% and only in 2017, OPV efficiency reached 13% [4]. A revolutionary study showed that materials based on OPV can show efficiency at the level of 17.3% make it possible to optimize the

prospects for the development of this direction [5]. At present, researchers of Photovoltaic polymers are so passionate about systems for increasing their energy efficiency that they completely ignore the fact that the currently developed Photovoltaic polymers are still synthesized by methods which cannot be called environmentally friendly [6]. One of the methods that needs to be done green is the bromination reaction, as it is the key step to getting the most commonly used for the construction of photovoltaic polymers of «building blocks».

Bromine-containing derivatives of aromatic and heteroaromatic compounds are the most important «building blocks» in the assembly of modern Photovoltaic Polymers (PV) [7]. While PV is being developed to produce «green» energy by converting sunlight to electricity, the reactions of obtaining

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brominated derivatives of building blocks described in modern articles are examples of obsolete, environmentally unfriendly technologies, in particular bromination by molecular bromine in the environment by concentrated hydrobromic acid [8, 9]. Currently, bromination methods are becoming increasingly widespread, in which bromine is generated directly during the reaction. For example, a method of the selective synthesis of 2-bromothiophene by bromination of thiophene with potassium bromate in hydrobromic acid is described [10]. The most widespread was bromination with a mixture of sodium or potassium salts of hydrobromic and bromic acid in the environment of strong acids, for example, concentrated hydrochloric acid [11]. These salts, which are the source of bromine, are white, crystalline substances that are relatively safe in storage, transport, and do not have any smell or irritating properties. The dry mixture of these salts is stable and can be stored for a long time. Wherein, bromine is stood out as a result of an oxidation-reduction reaction between these salts only in an acid environment:



The use of hydrochloric acid for carrying out the reaction is difficult for two reasons: a 37% solution of hydrochloric acid does not dissolve or poorly dissolve organic substances, and in some cases it may initiate side reactions, because of this from a technical point of view it is a poor solvent; secondly, hydrochloric acid causes corrosion of metals; contact with skin, respiratory tract, eyes causes irritation and the need to seek medical help. There are also questions related to how to dispose or regenerate hydrochloric acid if the reaction is scaled to an industrial scale.

Although the acetic acid also exudes an unpleasant odor, as well as hydrochloric acid, nevertheless, it is less toxic and has much less corrosive ability. Equally important is that acetic acid can be much more easily recycled or utilized than hydrochloric acid. Unlike a solution of hydrochloric acid, acetic acid dissolves the initial reagents and reaction products, including evolved water.

The calculation of the hazard rating of hydrochloric acid according to the Chem21 Solvent Selection Guide [12] showed that a 37% solution of hydrochloric acid has a combined effect, each of which is assigned a rating score. GHS data were taken from sources [13, 14]. So, the hydrochloric acid solution in relation to human health has the

following ratings: H315 (Causes skin irritation, 2 points), H319 (Causes serious eye irritation, 2 points), H335 (May cause respiratory irritation, 2 points), H318 (Causes serious eye damage, 4 points), H370 (Causes damage to organs, 6 points), H372 (Causes damage to your skin, prolonged or repeated exposure, 6 points), H314 (Causes severe skin burns and eye damage, 7 points). The environmental hazard rating is rated as H400 (Very toxic to aquatic life, 7 points). The total rating of the maximum values of the overall hazard H290 (May be corrosive to metals, 3 points), the hazard to human health H314 and the harm to the environment H400 is 17 points, which makes it possible to evaluate a solution of concentrated hydrochloric acid as a solvent that is totally unacceptable for use because of its danger. In the same paper [14], acetic acid was rated «between recommended and problematic». This rating position allows you to use acetic acid in any production and to perform any operations. In the same article, it is noted that acetic acid is a renewable source of raw materials. Thus, its use is fully consistent with the 1, 3, 7, and 10 principles of the Green Chemistry concept [15].

## 2. Experimental

Synthesis of 4, 4' - dibromo-1, 1'-biphenyl (1) was carried out by the following method. In a 100 ml round-bottomed flask containing a solution of 1.8 g (0.01 M) of 1,1'-biphenyl (5) in 20 ml of glacial acetic acid, 0.5 g portions were added over a period of one hour a dry mixture consisting of 3 g (0.02 mol) of sodium bromide and 3.34 g (0.02 mol) of potassium bromate at room temperature, while stirring on a magnetic stirrer. The reaction mixture was then heated with stirring for 8 h at a temperature of 60 °C, after which the reaction mixture was left until morning. The formed precipitate was filtered off, washed with warm water, the resulting precipitate was air-dried, then recrystallized from ethanol-benzene (10:1). White crystals were obtained. The mass of the dry residue before crystallization was 1,61 g,  $\omega = 43\%$ ,  $T_{m.p.} = 163\text{--}164\text{ }^\circ\text{C}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ): ( $\delta\text{H/ppm}$ ) 7.65 (d, 2H), 7.61 (d, 2H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ): ( $\delta\text{C/ppm}$ ) 122.1, 121.8, 130.5, 139.3.

Synthesis of 4,7-dibromo-2,1,3-benzothiadiazole (2). To the solution of 2,1,3-benzothiadiazole (3 g, 0.02 mol) in glacial acetic acid (45 ml), placed in a round bottom flask equipped with an effective reflux condenser, was added through a refrigerator, with stirring and heating to 60 °C in small portions,

a mixture of 6.42 g. NaBr (0.062 M) and 7.1 g. KBrO<sub>3</sub> (0.042 M) were stirred for 1 h. The synthesis was continued for 8 h. Then the mixture was stirred at reflux condenser for 2 h. The hot reaction mixture was filtered and the precipitate was washed several times with distilled water. Then the filtrate was cooled to further precipitate the product, filtered and the solid washed with water. The filtrate was poured into a solution of sodium thiosulfate Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (10% w/w) to remove excess of bromine. The obtained orange solid was recrystallized from ethanol and taken (2) as off-white needles (6.09 g, 94% yield). *T<sub>m.p.</sub>* = 185.5–187.5 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): (δH/ppm) 7.76 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): (δC/ppm) 152.9, 132.3, 113.9.

Synthesis of 2-bromothiophene (3) and 2,5-dibromothiophene (4) was carried out by the following method. In a 100 ml round-bottomed flask containing a solution of 1.68 g (0.02 M) of thiophene in 40 ml of glacial acetic acid, a dry mixture consisting of 6 g (0.04 mol) of sodium bromide and 6.68 g (0.04 mol) of potassium bromate at a temperature of no higher than 10 °C, while stirring on a magnetic stirrer. The mixture was stirred for 8 h, after which the reaction mixture was left until morning. Under the vacuum of the water jet pump, acetic acid was distilled off, 40 ml of tetra chloromethane and 4 g of dry, crushed sodium hydroxide were added to the mixture. The obtained mixture was heated at reflux for 4 h. After that, the precipitate was separated by filtration, and the filtrate was distilled with a reflux condenser. The yield of the product (6) was 0.9 g (*n*<sub>D</sub><sup>20</sup> 1.584, *t<sub>b.p.</sub>* = 150 °C; of the product (7) 1.1 g (*n*<sub>D</sub><sup>20</sup> 1.631, *t<sub>b.p.</sub>* = 210 °C);. <sup>1</sup>H NMR (6) (CDCl<sub>3</sub>): (δH/ppm) 7.43 (d, 1H), 6.72 (m, 1H), 6.91 (d, 1H) <sup>13</sup>C NMR (6) (CDCl<sub>3</sub>): (δC/ppm) 111.9, 130.3, 128.9., 128.4. <sup>1</sup>H NMR (7) (CDCl<sub>3</sub>): (δH/ppm) 6.65 (d, 2H); <sup>13</sup>C NMR (7) (CDCl<sub>3</sub>): (δC/ppm) 111.5, 130.2.

### 3. Results and discussion

It was found by us, that acetic acid can be successfully used for the bromination of 1,1'-biphenyl (5), 2,1,3-benzothiadiazole (6) and thiophene (7), heterocycles, which are actively used to create Photovoltaic Polymers. The reaction scheme is presented in Fig. 1.

When bromide mixture of bromide and potassium bromide (or sodium) mixture is added to acetic acid containing a brominated object, bromine is formed which reacts with bromination.

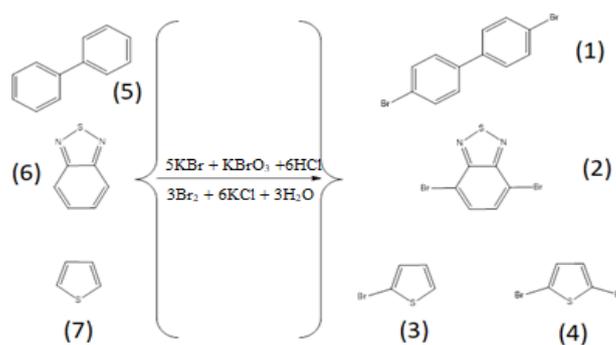


Fig. 1. Reaction scheme of bromination.

Besides of bromine, only potassium acetate and water are formed in this reaction. The reaction of bromination of substances (5) and (6) was carried out by heating brominated substances to 60 °C in acetic acid for 6–8 h with the regular addition of a dry mixture of bromide and potassium bromide. The yields of products (1) and (2) are comparable with the yields in the prototype techniques [1, 2]. Bromination of thiophene (7) was carried out at a temperature no higher than 10 °C. The yields of products (3) and (4) do not exceed 45%, partial refining of the reaction mixture is observed. Bromide and potassium bromate, from which bromine is formed by reaction with acetic acid, in normal conditions they are safe solids, with which it is comfortable and safe to work. The described method corresponds to the principles of the concept of «Green Chemistry» [15].

### 4. Conclusions

During the implementation of the project, the authors developed simple and comfortable bromination methods that lead to the building blocks of «Photovoltaic polymers» that are in demand for building such building blocks as: 4,4'-dibromo-1,1'-biphenyl (1), 4,7-dibromo-2,1,3-benzothiadiazole (2), 2-bromothiophene (3) and 2,5-dibromothiophene (4). All methods correspond to the principles of «green chemistry».

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