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New Method of the Synthesis of *N,N'*-Diphenyl-1,4-benzoquinone Diimine

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Abstract—A method of synthesis of *N,N'*-diphenyl-1,4-benzoquinone diimine by oxidation of *N,N'*-diphenyl-1,4-phenylenediamine with potassium permanganate in acetone at room temperature was developed. The procedure of isolation and exhaustive purification of the product includes recrystallization from a number of solvents and elimination of impurities on a short column packed with silica gel.

Keywords: *N,N'*-diphenyl-1,4-benzoquinone diimine, synthesis, oxidation, *N,N'*-diphenyl-1,4-phenylenediamine, potassium permanganate

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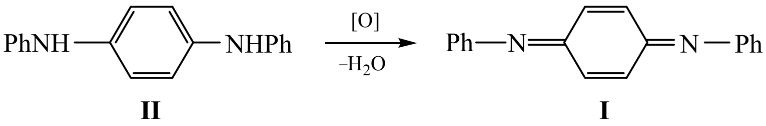
Increased interest attracted by quinonemono- and quinone diimines is due to their high reactivity [1, 2] and biological activity. One of the metabolites of the well-known analgesic *N*-(4-hydroxyphenyl)acetamide (paracetamol) is *N*-acetyl-1,4-benzoquinone imine [3] causing liver necrosis [4]. Some quinone imines, on the contrary, exert a therapeutic effect. For example, naphthoquinone imines exhibit an antitubercular activity [5].

Quinone imines act as antioxidants in production of a number of polymers, rubbers, and vulcanized rubbers [6–9]. In recent years, chain reactions involving quinone imines were discovered, in particular, reversible reactions of quinone imines with hydroquinones [10, 11], as well as reactions of quinone imines with thiols [12].

Being commercially unavailable, quinone imines must be prepared in the laboratory. We repeatedly synthesized quinone imines, in particular, *N,N'*-diphenyl-1,4-benzoquinone diimine (**I**).

The kinetics and mechanism of chain reactions involving quinone imines are strongly dependent on the purity of the chemicals used, so quinone imines should satisfy exceptionally stringent requirements in terms of their purity. Taking this into consideration, we developed a new method of synthesis and purification of compound **I**, also applicable for preparation of other quinone imines.

Compound **I** was prepared for the fist time (in a low yield) in 1886 by oxidation of an aqueous alkaline solution of diphenylamine with potassium permanganate [13]. However, this procedure was subsequently abandoned and replaced by methods based typically on oxidation of *N,N'*-diphenyl-1,4-phenylenediamine (**II**) with some oxidant.



The initially chosen oxidant was oxygen which was bubbled through alkaline alcoholic solutions of compound **II**, brought to boiling [14]. The currently used processes are based on solutions of this compound in an 8% solution of potassium methylate in methanol, through which a 1 : 11 oxygen-nitrogen mixture, instead of oxygen, is bubbled [15]. Thereby, the synthesis temperature can be decreased to 30°C. In [16], oxidation of compound **II** by atmospheric oxygen in the presence of solid NaOH for 6 h was described;

in the course of the synthesis the temperature was increased from 130 to 180°C.

The use of another oxidant, hydrogen peroxide, which was added in portions to a refluxing alcoholic solution of diamine **II**, was described in [14]. The procedure of oxidation of 1,4-phenylenediamines with hydrogen peroxide in the presence of a catalyst [copper(II) oxide] was used for the preparation not only of compound **I** but also of a number of other quinone diimines with peripheral ring substitution [17].

Quinone diimine **I** was isolated from the products of AIBN decomposition in the presence of compound **II** (chlorobenzene, atmospheric oxygen) [18]. The laboriousness of this method involving separation of a complex mixture of products from a radical reaction prevented its widespread application for producing other quinone imines. The method described in [19] may also be mentioned where compound **I** and a number of other substituted quinone diimines were prepared by treating a solution of diamine **II** with bromine in methanol containing potassium methylate.

The preparation of quinone diimine **I** by oxidation of compound **II** (a solution in benzene [20]) with an aqueous solution of potassium ferricyanide was also described. The reaction proceeded slowly, and the yield was low. Nevertheless, this method was also used for preparation of some other quinone imines, in particular, *N*-phenyl-*N*'-isopropyl-1,4-quinone diimine and *N*-phenyl-*N*'-cyclohexyl-1,4-quinone diimine [21]. In [8] the use of ether instead of benzene as the organic phase in the synthesis of *N*-phenyl-*N*'-cyclohexyl-1,4-quinone diimine was suggested, whereby the process was accelerated.

In [22], the preparation of quinone imines by oxidation of appropriate diamines in acetonitrile with a sodium hypochlorite solution was described. The main problems associated with the isolation of the reaction products were overcome by carrying out extraction with toluene after addition of water.

Also noteworthy are the methods of synthesizing quinone imines by oxidation of the appropriate amines with heavy metal oxides: HgO [23, 24], Ag_2O [21], and freshly prepared MnO_2 [25]. Special mention deserves the method proposed by Piccard [26], where compound **II** was oxidized by chromic acid solution in acetic acid. Quinone imines are formed in nearly quantitative yields, and the main difficulties consist in their isolation and purification.

The synthesis method we developed is distinguished among other methods by its simplicity. It even seems surprising that potassium permanganate was not previously used for oxidation of diamine **II**. The synthesis procedure is carried out at room temperature and does not require special equipment and expensive chemicals. Analytical grade acetone and aromatic solvents may be used without further purification, and purification of analytically grade methanol used for recrystallization may be restricted to the standard procedure [27]. It should be noted that the main goal we set for ourselves was to obtain high-purity compound **I** suitable for experimental studies of the kinetic features of chain reactions involving quinone imines. In this connection, we deliberately sacrificed quantity for the sake of quality of the substance when carrying out some manipulations.

EXPERIMENTAL

***N,N*'-Diphenyl-1,4-benzoquinone diimine I.** To 50 mL of an acetone solution of 2.0 g (7.7 mmol) of commercial *N,N*'-diphenyl-1,4-phenylenediamine **II** (Fluka, 97%), thoroughly freed from impurities by the procedure described in [28], a solution of 0.92 g (6.0 mmol) of analytically pure $KMnO_4$ in 100 mL of acetone was added while stirring at room temperature during 30 min. The resulting MnO_2 precipitate was filtered off under reduced pressure and washed twice on the filter with 10-mL portions of acetone. The filtrate was evaporated to ~50 mL under a stream of air at room temperature and heated to boiling for dissolution of the precipitated crystals of compound **I**, after which the solution was cooled to –18°C. The crystals were filtered off and washed on the filter with two 5-mL portions of cold acetone, dried to dryness in air at room temperature, recrystallized from toluene, washed on the filter with 10 mL of cold toluene, and dried. The toluene mother liquor, combined with the dried residues of the acetone mother liquor from the preceding crystallization, was heated to nearly boiling, after which the hot solution was decanted from the inorganic impurities while stirring. The solution was evaporated to ~5 mL at room temperature under a stream of air, and the mother liquor was removed with a pipette from the precipitated crystals which were further recrystallized twice from toluene. The resulting crystals of compound **I** were combined with the crystals obtained by recrystallization from acetone, after which toluene was added until the crystals completely dissolved. The resulting nearly saturated solution (250–350 mL) was passed through a ~5 cmthick SiO_2–L silica gel (Chemapol, 100–160 μm) layer in a glass column. The fraction containing compound **I** was collected when the solution coming out of the column turned orange. After the solution had completely passed through SiO_2, toluene was poured into the column, and elution of compound **I** was continued until the front of a bright crimson polar impurity reached the column outlet. The solvent was removed from the eluate by rotary evaporation, and the crystals were filtered off, washed with a toluene-hexane mixture (1 : 1, 2 × 20 mL), and dried in air at room temperature. Next, ~350 mL of methanol was added to the crystals and heated to nearly boiling, after which ~2 mL of chloroform was added in small portions while stirring until complete dissolution. The solution was slowly cooled to –18°C, and the resulting crystals were filtered off, washed with cold methanol, and dried at room temperature, and then in a vacuum. The melting point was determined on a Boëtius micro-hot plate (RNMK 05 model). Yield ~1.2 g (~60%), mp 185–186°C (cf. 176–180 [13, 26], 181–183 [15, 19], 183–185 [18], 181.5–182.5°C [24]). The purity of the resulting compound **I** was tested by comparing its IR spectrum (KBr) and absorption spectrum in the visible region (toluene) [λ_{max} 449 nm, ε 6870 L mol^{-1} cm^{-1}] with the available published data [24, 29, 30]. Found, %: C 83.82; H 5.27; N 10.91. $C_{18}H_{14}N_2$. Calculated, %: C 83.69; H 5.46; N 10.84.

The IR spectra and the absorption spectra were recorded on a Specord 75 IR and a Specord M 40 instruments, respectively.

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