

SHORT
COMMUNICATIONSFacile Iodination of Aromatic Compounds
Having Electron-Withdrawing Substituents. Generation
of Triiodine Cation in the System Tetra-*N*-iodoglycoluril–
Iodine–Sulfuric AcidV. K. Chaikovskii^a, A. A. Funk^a, V. D. Filimonov^a, T. V. Petrenko^b, and T. S. Kets^c^a Tomsk Polytechnical University, pr. Lenina 30, Tomsk, 634050 Russia
e-mail: clg@mail.ru^b Institute of Petroleum Chemistry, Siberian Division, Russian Academy of Sciences, Tomsk, Russia^c Tomsk State Pedagogical University, Tomsk, Russia

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In the middle of the past century several methods for the generation of I_3^+ ion by reaction of iodine with oxidants in oleum or sulfuric acid were proposed and studied [1, 2]. It was shown that triiodine cation in solution exhibits enhanced electrophilicity and that they are capable of iodinating benzene derivatives having electron-withdrawing substituents [3, 4].

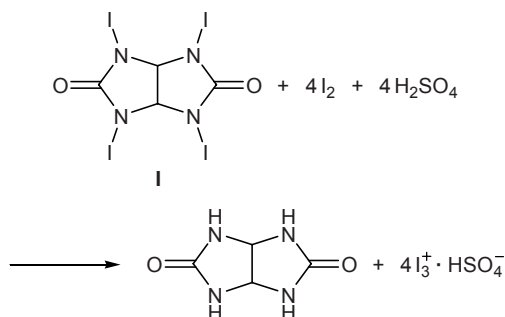
On the basis of spectral data and quantum-chemical calculations we previously presumed [5–9] that dissolution of *N*-iodo imides in sulfuric acid could give rise to triiodine cation I_3^+ together with iodine(I) hydrogen sulfate (IOSO₃H). With a view to get additional support to the above assumption we made an attempt to obtain a solution of I_3^+ by reaction of tetra-*N*-iodoglycoluril (**I**, 1,3,4,6-tetraiodoperhydroimidazo[4,5-*d*]imidazole-2,5-dione) with iodine in sulfuric acid. As a result, we have developed an effective alternative way for the generation of I_3^+ . A solution containing I_3^+ is

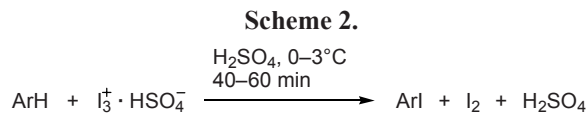
readily formed by gradually adding compound **I** to a suspension of finely ground iodine in sulfuric acid ($d = 1.815\text{--}1.834\text{ g/cm}^3$) under stirring at 0–3°C (Scheme 1).

We believe that the reaction of compound **I** with I_2 in sulfuric acid leads to quantitative formation of highly reactive iodinating intermediate $I_3^+ \cdot HSO_4^-$. The process ensures fast generation of I_3^+ in a high concentration. The obtained solution is stable, it has a dark brown color and absorbs at λ 453 and 291 nm, which is consistent with the electronic absorption spectrum of I_3^+ given in [1]. The reagent readily reacts with nitrobenzene (**IIa**) at 0–3°C in 40 min to give 3-iodonitrobenzene (**IIb**) in 82% yield. Under analogous temperature conditions, one or two iodine atoms can be introduced in 45–60 min into molecules of 4- and 2-nitrotoluenes **IIIa** and **IVa**, benzaldehyde (**Va**), benzoic acid (**VIa**), 4-fluorobenzoic acid (**VIIa**), benzophenone (**VIIIa**), benzil (**IXa**), and fluorenone (**Xa**); the corresponding products, 2-iodo-4-nitrotoluene (**IIIb**), 2,6-diiodo-4-nitrotoluene (**IIIc**), 4-iodo-2-nitrotoluene (**IVb**), 3-iodobenzaldehyde (**Vb**), 3-iodobenzoic acid (**VIb**), 4-fluoro-3-iodobenzoic acid (**VIIb**), 3,3'-diiodobenzophenone (**VIIIb**), 3,3'-diiodobenzil (**IXb**), and 2,7-diiodofluorenone (**Xb**), were isolated in 42–70% yield.

The reactions with aromatic substrates are accompanied by appreciable decoloration of the reaction mixture. During the process, the complex $I_3^+ \cdot HSO_4^-$

Scheme 1.





decomposes to give molecular iodine (Scheme 2) which separates from the solution; it can be filtered off and reused.

According to the GC–MS data, the iodination of nitrobenzene (**IIa**) was characterized by complete conversion of the substrate. It should be noted that, unlike iodination with a solution of **I** in sulfuric acid in the absence of molecular iodine [5], the iodination of arenes with I_3^+ generated from compound **I** and I_2 in sulfuric acid requires no double excess of active iodine in **I**. This is very important, taking into account high cost of reagent **I**.

Preparation of a solution containing triiodine cation. Tetraiodoglycoluril **I** was synthesized according to the procedure described in [10]. A suspension of 1.016 g (4 mmol) of finely ground iodine in 30 ml of sulfuric acid ($d = 1.815 \text{ g/cm}^3$) was cooled to $0-3^\circ\text{C}$ using an ice–water bath, and 0.646 g (1 mmol) of compound **I** was added in four portions under vigorous stirring. The mixture was stirred for ~30 min at room temperature (until the iodine dissolved completely) to obtain a dark brown homogeneous solution. A 0.01-ml portion of the solution of I_3^+ was diluted with 2 ml of sulfuric acid, and its electronic absorption spectrum showed maxima at λ 453 and 291 nm.

Typical procedure for the iodination of aromatic compounds IIa–Xa with I_3^+ . Arene **IIa–VIIa**, 4 mmol, was added to 30 ml of a preliminarily prepared solution of I_3^+ , cooled to $0-3^\circ\text{C}$, and the mixture was stirred for 40–60 min. In the synthesis of diiodo derivatives **IIIc** and **VIIIb–Xb**, the amount of the substrate was reduced by half (2 mmol). The mixture was poured onto ice and washed with a 2% solution of Na_2SO_3 . Products **IIIc** and **VIb–Xb** were separated by filtration

and purified by recrystallization. Compounds **IIb–Vb** were isolated by extraction into methylene chloride, the extract was dried over CaCl_2 , the solvent was distilled off, and the residue was purified by recrystallization.

The electronic absorption spectra were measured on a Uvikon-943 spectrophotometer using 10-mm cells. The progress of reactions and the purity of products were monitored by TLC on Sorbfil plates (detection under UV light). The structure of the iodination products was confirmed by spectral and analytical methods and by comparing with authentic samples.

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