

SHORT
COMMUNICATIONS

Synthesis of *N*-Iodosuccinimide and Its Application in H₂SO₄ as Efficient Iodination Reagent for Deactivated Aromatic Compounds*

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N-Iodosuccinimide (**I**) found application in organic synthesis for iodination of ketones, aldehydes, and alkenes [1, 2]. For a long time it was presumed to be able to iodinate in organic solvents (alcohols, dioxane, acetonitrile, dichloromethane) only activated or slightly deactivated arenes (phenol ethers, iodobenzene etc.) [3-6]. The electrophilic activity of iododerivative **I** is sharply increased in CF₃SO₃H, and then it can efficiently iodinate nitrobenzene and a number of the other deactivated aromatic compounds [7].

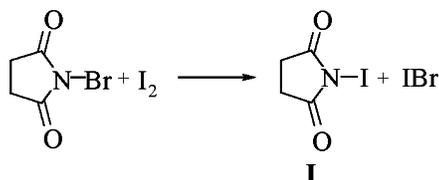
We have formerly established that superactive electrophilic iodine capable to easily iodinate strongly deactivated arenes is formed in sulfuric acid from iodine monochloride and silver sulfate (reagent I⁺) [8, 9] or from 2,4,6,8-tetraiodo-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione (tetraiodoglycoluril) [10].

On these grounds we presumed that iodide **I** should generate highly electrophilic iodine in sulfuric acid. Actually it turned out that iododerivative **I** in H₂SO₄ readily iodinated nitrobenzene at 20°C within 20 min or at 0°C within 1.5 h affording 3-iodonitrobenzene (**II**) in 77-79% yield. The disadvantage of the method consists in the necessity to use a double excess of compound **I** as compared with the calculated amount. At equimolar reagents ratio a complete conversion of nitrobenzene into 3-iodonitrobenzene (**II**) takes 20 h at 20°C.

Thus the result obtained considerably extends the opportunities of iodide **I** application as iodinating reagent. However its wide application is limited since it is an expensive reagent. We attempted to find an efficient procedure for preparation of compound **I** to

make it more accessible. A usual preparation of compound **I** is from succinimide with the use of silver hydroxide and iodine [11]. Although the reaction product is of good quality (mp 200-201°C) the preparation procedure is multistage and expensive. The synthesis of compound **I** from the sodium salt of succinimide and iodine monochloride [12] provided the target compound of relatively low quality (mp 187-190°C). It is known that iodide **I** formed on long boiling (48 h) of *N*-bromosuccinimide with excess iodine in 1,2-dichloroethane [13].

We found that iododerivative **I** readily formed at heating equimolar amounts of *N*-bromosuccinimide and iodine in CCl₄ to 40-55°C for 1 h in nearly quantitative yield.



Obviously the acceleration of reaction in going from solution in 1,2-dichloroethane to CCl₄ is due to the known higher ability of the latter to generate free radicals that initiate the exchange process. It should be noted that reaction occurs readily only with unpurified *N*-bromosuccinimide that has light-yellow color. After recrystallization from water or nitromethane the colorless *N*-bromosuccinimide reacts with iodine only in boiling CCl₄ and significantly slower (2 h) providing iodide **I** in low yield and of reduced properties. This fact indicates that occluded bromine present as microcomponent plays a promotor role; however addition of a little molecular bromine (5-10 mol%) to the recrystallized *N*-bromosuccinimide hardly affects the course of the process.

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N-Iodosuccinimide (I). To a mixture of 5 g of *N*-bromosuccinimide of "pure" grade and 7.5 g of ground into a powder iodine was added 10 ml of CCl₄, and the mixture was stirred at 50°C for 30 min till it became tick. In the course of the process the reaction mixture became orange-brown due to formation of iodine monobromide,. Then was added 20 ml of CCl₄ more, and the reaction mixture was stirred at 40–50°C for another 30 min. The residue was filtered off and kept under fume hood to remove the formed iodine monobromide. Yield of compound **I** 6.3 g (98%), mp 192–195°C. For further purification the product was dissolved in 7 ml dioxane at boiling and was added 3.5 ml of CCl₄. The solution was cooled to 20°C, the precipitate was filtered off and dried in air, yield 5.1 g (80%), mp 200–201°C (mp 200–201°C [11]). Found, %: C 21.52; H 1.70; I 56.12. C₄H₄INO₂. Calculated, %: C 21.33; H 1.78; I 56.44.

3-Iodonitrobenzene (II). To 2.25 g of iodide **I** was added 30 ml of 90% H₂SO₄ preliminary cooled to 0–5°C, and the mixture was stirred at room temperature for 20–30 min till iodide **I** completely dissolved. To the solution obtained was added 0.62 g of nitrobenzene, and the reaction mixture was stirred for 20 min at 20°C. Then it was poured into 100 ml of ice water and washed with water solution of Na₂SO₃. The reaction product **II** was extracted into CH₂Cl₂, the extract was dried on CaCl₂, the solvent was distilled off, and compound **II** was crystallized from ethanol. Yield 0.99 g (79%), mp 35–36°C (mp 36–37°C [7]).

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