

Optimized syntheses of iodylarenes from iodoarenes, with sodium periodate as the oxidant. Part II

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Dedicated to Professor Anastasios Varvoglis on his 65th birthday
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Abstract

An improved method is reported for optimized preparations of iodylarenes, ArIO_2 , from iodoarenes, ArI , using NaIO_4 as the oxidant dissolved in boiling 30% (v:v) aq. CH_3COOH solutions. The former reaction times, reported in Part I,¹ were shortened from 8-16 hours to 3-6 hours, with preserving the same good yields and high purities of the *crude* final products, ArIO_2 . A considerably improved method of preparing „2-iodosylbenzoic acid” is also reported in this paper. See also our [Warning](#) submitted in Experimental.

Keywords: Iodylarenes, 2-iodosylbenzoic acid, iodoarenes, sodium periodate, oxidation

Introduction

During the past 20 years, iodylarenes, ArIO_2 , the aromatic compounds of *iodine(V)*, have widely been used in organic synthesis as mild and very selective oxidants. The most important iodylarenes are: iodylbenzene, 4-(*t*-butyl)iodylbenzene, "2-iodylbenzoic acid" [i. e. 1-hydroxy-1,2-benziodoxol-3-(1*H*)-one 1-oxide, **IBX**], and its derivative named the Dess-Martin reagent [1,1,1-triacetoxy-1,2-benziodoxol-3-(1*H*)-one].²

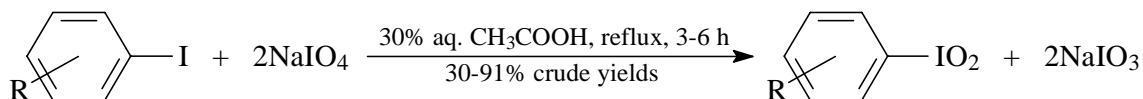
It is known that large quantities of some organophosphorus poisons, viz. Sarin, Soman, Tabun, VX, or Russian-VX are still stockpiled in a number of countries around the world, and their destruction requires the use of environmentally friendly processes. It has been discovered that the conjugate bases of 2-iodosyl- and 2-iodylbenzoic acids, i.e. 2-iodosyl- and 2-iodylbenzoates, may successfully be used for the degradation of organophosphorus substrates, including those mentioned above.³ This is why we believe that our novel easy and fairly effective syntheses of 2-iodosyl- or 2-iodylbenzoic acids may be of a practical interest.

In Part I,¹ we reported a new method for preparing iodylarenes from iodoarenes, in boiling and vigorously stirred *neutral* aqueous sodium periodate solutions. These reactions proceeded *within 8-16 hours* and gave ArIO₂ in 58-91% *crude* yields, having 97-99% purities established iodometrically.⁴ We have recently tried, in vain, to accelerate these reactions *with microwave irradiation*.

The aim of Part II has been to notably shorten the former prolonged reaction times,¹ but with preserving the former good yields and high purities of the *crude* final products, ArIO₂ – which next may be used *as such*, without purification, in subsequent reactions. We have also attempted to considerably improve our former synthesis¹ of „2-iodosylbenzoic acid”.

Results and Discussion

Recently, in our laboratory we have devised an improved method for optimized preparations of ArIO₂ from ArI. We observed that when the aforementioned boiling reaction mixtures were acidified with dilute H₂SO₄, the *yellowish* iodosylarenes, ArIO, were the main products of the reactions. When we used varied boiling aqueous CH₃COOH solutions, the initially precipitated out yellowish ArIO, after 0.5-1.5 h were transformed into colorless ArIO₂. According to these observations, we previously suggested¹ that the reactions underwent in two steps: ArI are oxidized to only ArIO, and the latter ones are readily *thermally disproportionated* to give ArI and ArIO₂. We established experimentally that the optimum concentration of aqueous CH₃COOH solutions for preparing ArIO₂ was just **30% (v:v)**. Using this binary *acidic* solvent, we considerably shortened the reaction times *to 3 – 6 hours* and, in some cases, we also increased the *crude* yields. Iodometric titrations⁴ showed 96-99% purities of the *crude* iodylarenes obtained.



Scheme 1

R - see Table 1.

Table 1. The reaction times, crude yields, and melting points (uncorrected) for the recrystallized ArIO₂ (Scheme 1)

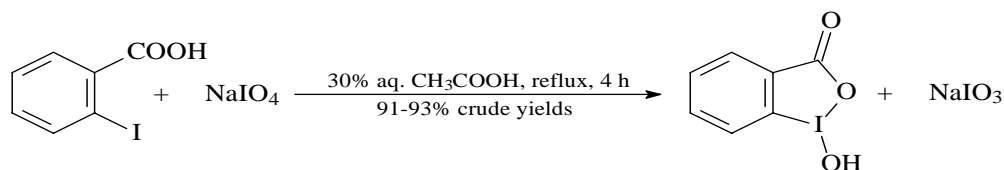
R	Time [h] ^{a)}	Crude yield [%]	Mp [°C]	Lit. mp [°C]
H	4	76	235 (expl.)	235 (expl.) ¹
	6	84		

2-CH ₃	4	70	206-207	208 ¹
3-CH ₃	3(+1)	75	218 (expl.)	220 (expl.) ¹
4-CH ₃	3(+1)	84	227 (expl.)	229 (dec.) ¹
2-Cl	5(+1)	40	205-206	203 (expl.) ¹
3-Cl	3(+1)	75	231 (expl.)	233 (expl.) ¹
4-Cl	3(+1)	87	240 (expl.)	232 (expl.) 243 (expl.) ⁵
2-NO ₂	3(+1)	54	212 (expl.)	210 (expl.) ⁵
3-NO ₂	3(+1.5)	84	215 (expl.)	214 (dec.) ¹
4-NO ₂	3(+1)	58	214 (expl.)	215 (dec.) ¹
3-F	4	91	226-227	226 ⁵
4-F	2(+1)	87	245 (expl.)	248 ¹
4-Br	3(+1.5)	81	236	231 (expl.) 240 (expl.) ⁵
2,4-(CH ₃) ₂	4	54	194 (expl.)	195 ⁵
2,4-Cl ₂	3(+1)	30	223 (expl.)	225 ⁵

Note: Satisfactory microanalyses, I% ± 0.3 , were obtained for the purified ArIO₂; their IR spectra were the very same as those reported in Part I.¹

^a The reaction times *after adding* an additional volume of boiling water (20 mL) are given in parentheses.

2-Iodobenzoic acid, after 4 hours of its boiling with a solution of NaIO₄ in 30% (v:v) aq. CH₃COOH, gave the nearly pure (98-99%), colorless „2-iodosylbenzoic acid” [its stable cyclic tautomeric form is named: 1-hydroxy-1,2-benziodoxol-3(1*H*)-one] in 91-93% *crude* yields; for more details see Experimental, and cf. Part I.¹ However, 3- and 4-iodobenzoic acids, reacted similarly as 2-iodobenzoic acid, gave only *mixtures* of the corresponding iodyl- and iodosylbenzoic acids; such mixtures, analyzed iodometrically,⁴ may also be used for the degradation of organophosphorus substrates. See Part I¹ for the effective methods of preparing the *crude* 2-, 3- and 4-iodylbenzoic acids, all having 98-99% purities established iodometrically.⁴



Scheme 2

Conclusions

From the above experiments it is seen that our preliminary aims (*vide supra*) were successfully attained in the present Part II. It should be emphasized that all our *crude* final products, ArIO₂

and 2-OIC₆H₄COOH, had always high purities (96-99%), hence they may be used as such, *without purification*, in all possible subsequent reactions. Our **Warning** (see Experimental) evidences that even recrystallizations of ArIO₂ from boiling water may sometimes be *hazardous*, particularly when they are *scaled up*; they are also always connected with unavoidable *crystallization losses*.

Experimental Section

General Procedures. All the reagents and solvents were commercial (Aldrich, Fluka), and were used without purification. Chemical structures of the purified compounds in Table 1 were confirmed by satisfactory microanalyses obtained at the Institute of Organic Chemistry, the Polish Academy of Sciences, Warsaw, where also the IR spectra were recorded.

We have observed that melting/decomposition points of many ArIO₂ are rather *uncertain*, depending not only upon the purity of crude or purified products prepared, but also *upon the rate of their heating* during the melting point determinations; this is why their melting points reported in the literature^{1,5,6} often differ significantly. The melting points of ArIO₂ (Table 1) were uncorrected, and often accompanied by explosion. They were measured as follows: after an approximate m.p. had been taken in an open capillary tube, a new sample was introduced about 10 °C below this point, and the temperature was raised at a rate of 10 °C min⁻¹. This was repeated unless consistent results were attained.

Optimized procedures for preparing iodylarenes from iodoarenes

NaIO₄ (4.70 g, 22 mmol, 10% excess) was suspended in 30% (v:v) aq. AcOH (20 mL). An appropriate *iodoarene* (10 mmol) was added (for steam-volatile ArI, a few drops of *toluene* were also added; see Part I¹ for the explanation). The mixtures were *vigorously stirred* and refluxed for 2-6 h. In such cases, when the mixtures were still yellowish after this time, 20 mL of boiling water was added, and the resulting mixtures were further stirred and refluxed for 1-1.5 h (see Table 1). Next, the temperature was lowered to r. t. After 1 h, the crude products were collected by filtration, washed on the filter with ice water (3 x 10 mL) and acetone (3 x 10 mL), and air-dried *in the dark*. As previously,¹ small samples of the crude ArIO₂ were recrystallized, *with effective stirring*, from boiling water to obtain the analytical specimens.

Optimized procedure for preparing "2-iodosylbenzoic acid", i.e. 1-Hydroxy-1,2-benziiodoxol-3(1H)-one. NaIO₄ (2.25 g, 10.5 mmol; 5% excess) and 2-iodobenzoic acid (2.48 g, 10 mmol) were suspended in 30% (v:v) aq. AcOH (15 mL). The mixture was vigorously stirred and refluxed for 4 h. Next, the reaction mixture was diluted with cold water (50 mL) and cooled to r. t. After 1 h, the crude product was collected by filtration, washed on the filter with ice water (3 x 10 mL) and acetone (3 x 10 mL), and air-dried in the dark to give 91-93% yields. The colorless crude products thus obtained repeatedly were analyzed iodometrically⁴ to show 98-99% purities,

m.p. 254 °C (dec.); for the purified compound, m.p. 256 °C (dec.) (recrystallized, with stirring, from boiling water); m.ps. 234 °C (dec.) and 260 °C (dec.) were reported.^{1,5,6}

For C₇H₅IO₃ calcd C, 31.85; H, 1.91; I, 48.06%; for the purified compound found: C, 31.8; H, 2.0; I, 47.9%; for the crude product found: C, 32.0; H, 2.1; I, 47.9%.

Warning

Explosion during the recrystallization of 3-iodyltoluene from boiling water. Dry iodylarenes, ArIO₂, are generally *hazardous* compounds, which may explode upon impact, by scratching them with a spatula, on heating under confinement, etc.² *They should always be handled with care*, even during their preparations by oxidative reactions, or when they are purified by recrystallization from boiling water (*vide infra*).

In the course of our preparations of numerous ArIO₂ from the corresponding ArI, we recrystallized *crude* ArIO₂ from boiling water, *always with vigorous stirring*, to obtain the analytical specimens. But for a first time, a violent explosion occurred during the recrystallization of ca. 2 g of 3-iodyltoluene from boiling water. The blast of the explosion was such that fragments of the glassware scratched a transparent security shield made of Plexiglas, while a nest-shaped electric heater coated with asbestos was demolished. No one in the laboratory suffered injuries, due to the presence of the shield.

After the accident, we scrutinized a possible cause of the explosion. We came to the conclusion that it had probably been due to *ineffective stirring* the boiling biphasic system. It is known² that solid ArIO₂ has a polymeric nature, which makes it insoluble in most ordinary solvents, except water. During preparation and recrystallization, the densely-packed heavy crystals of ArIO₂ tend to settle down and to adhere to the walls of round-bottomed flasks, if the stirring is ineffective. Because the external electric heating of the flask was applied, hence *local overheating* the solid ArIO₂, adhering tightly to *hot* walls of the flask, resulted in the explosion. Hence, very effective stirrers, e.g. such as that of the Hershberg-type,⁷ should be used, which scrape out and stir the solids clinging obstinately to the walls of the used vessels. Also during the preparations of ArIO₂ from ArI, a very efficient stirring should be applied to sustain the heavy ArIO₂ crystals in the form of a *suspension* in the bulk of a boiled liquid phase heated externally.

Our preliminary results were presented at the Sixth Electronic Conference on Synthetic Organic Chemistry (ECSOC-6, <http://www.mdpi.net/ecsoc-6/>), September 1-30, 2002 (paper AO14).

References and Notes

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