



# Iodonium metathesis reactions of unreactive aryl iodides



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## ABSTRACT

Aryl iodides that are unreactive toward various diaryliodonium triflates undergo metathesis reaction with  $\lambda^3$ -iodanes based on a highly nucleofugal aryl iodide such as 2-iodothiophene. Examples of such reactive iodanes include phenyl(2-thienyl)iodonium triflate and bis-(2-thienyl)iodonium triflate. This observation provides support for a mechanistic hypothesis advanced earlier.

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## 1. Introduction

The iodonium metathesis reaction<sup>1</sup> involves the transfer of one or both aryl groups of a diaryliodonium triflate, **1** (a  $\lambda^3$ -iodane), to an external aryl iodide, resulting in formation of a new diaryliodonium triflate, **2** (Scheme 1). This occurs upon heating a solution of the reactants in a moderately polar, poorly Lewis basic solvent, such as 1,2-dichloroethane (DCE), and in the absence of any catalyst. In some cases, the reactants are converted substantially into a single product of the type **2**, although more commonly a mixture of  $\lambda^3$ -iodanes, including the starting diaryliodonium triflate, is obtained. The fact that iodonium metathesis occurs at all constitutes a novel aspect of the chemistry of diaryliodonium species.<sup>1,2</sup>

Whereas certain pairs of reactants undergo metathesis as per the above, others do not. For instance, Ph<sub>2</sub>IOTf reacts readily with 4-iodotoluene, 1-iodonaphthalene, or 4-iodoanisole, less so with 4-halo-iodobenzenes,<sup>3</sup> and not at all with ethyl 4-iodobenzoate, 4-trifluoromethyl-iodobenzene, or 4-nitro-iodobenzene. A plausible explanation for this is as follows.

Computational methods indicate that the I-atom in an aryl iodide sustains a fractional positive charge. Earlier,<sup>1</sup> this (+)-charge was estimated for various aryl iodides as the geometric mean<sup>4</sup> of values calculated after full geometry optimization by four semi-empirical methods: MNDO, MNDO-d, AM1 and PM3.<sup>5</sup> However,

values calculated by MNDO-d closely approximate the geometric means (average deviation = 0.001 e).<sup>6</sup> Therefore, all work described herein is based on I-(+)-charges calculated by MNDO-d.<sup>5</sup> Pertinent data appear in Table 1.

The presumed reason why the first 4 iodoarenes in Table 1 readily participate in metathesis, while the others do not (“unreactive” iodides) is that iodonium metathesis occurs so that a more I-nucleophilic (=less I-positive) iodide displaces a less I-nucleophilic (=more I-positive) one.<sup>7</sup> If so, unreactive aryl iodides may well undergo metathesis with diaryliodonium species incorporating particularly nucleofugal (strongly I-positive) aryl iodides. Herein, we elaborate the ramifications of this surmise and present results that provide a preliminary mechanistic picture for the reaction.

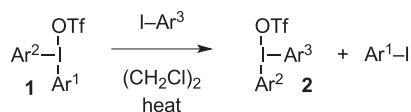
## 2. Results and discussion

The iodonium metathesis reaction is unlikely to proceed in an S<sub>N</sub>Ar mode. Such a mechanism fails to account for various aspects of the process,<sup>1</sup> which instead may commence with the reversible dissociation of **1** into a free iodonium ion **3**.<sup>8</sup> A reversible nucleophilic addition of an external aryl iodide, Ar<sup>3</sup>-I,<sup>9</sup> to **3** leads to complex **4**. This reactive intermediate may undergo reductive elimination of, e.g., Ar<sup>1</sup>-I (cf. **5**) to give **6**, which re-associates with triflate ion to form **2** (Scheme 2).<sup>10</sup>

An iodine atom undoubtedly acquires additional positive character as it advances from the monovalent to the polyvalent state. This would be especially true for free diaryliodonium ions such as **3** (or **6**). The data of Scheme 3, which provides a crude estimate

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Scheme 1. The iodonium metathesis reaction.

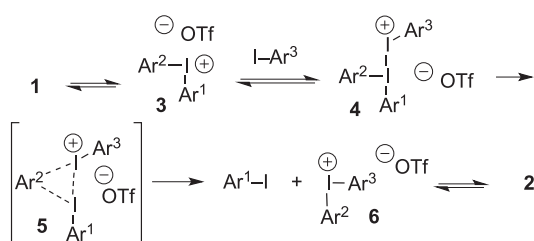
(MNDO-d)<sup>11</sup> of the I-(+)-charge on representative diaryliodonium ions, seem to support such a hypothesis.

The electronegative nature of the iodine atom surely opposes the accumulation of an increasing extent of (+)-charge on it. Consequently, a more I-positive polyvalent iodine species is more energetic than a less I-positive one, and it will tend to undergo changes leading to less I-positive products. In the case of a  $\lambda^3$ -iodane such as **1** or **4**, an increasing extent of I-(+)-charge on the I-atom will accelerate the rate of reductive elimination of the more I-philic Ar-I. Furthermore, increasingly I-positive (more electrophilic) diaryliodonium ions would be expected to associate increasingly readily even with weakly nucleophilic aryl iodides, leading to complexes **4**, which may then undergo reductive

**Table 1**  
Calculated charge on the I-atom of various aryl iodides (MNDO-d).<sup>5</sup>

Iodoarene	(+)-charge on I ( $e^a$ )	
iodomesitylene	0.060	nucleophilic character
1-iodonaphthalene	0.067	
iodobenzene	0.075	
4-iodoanisole	0.076	
4-iodotoluene	0.077	
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4-chloro-iodobenzene	0.089	"unreactive" iodides
1,4-diiodobenzene	0.091	
4-bromo-iodobenzene	0.091	
4-fluoroiodobenzene	0.091	
methyl-4-iodobenzoate	0.095	
3,5-di(carbomethoxy)iodobenzene	0.107	
4-trifluoromethyl-iodobenzene	0.108	
4-nitro-iodobenzene	0.118	
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2-iodothiophene	0.154	nucleofugal character

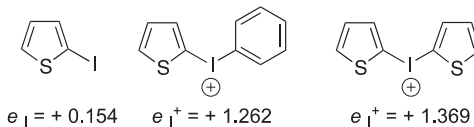
<sup>a</sup> Units of electron charge calculated after geometry optimization.



Scheme 2. Presumed mechanism of the iodonium metathesis reaction.



R = H: $e_I = +0.075$	R = H: $e_{I^+} = +1.146$
R = Me: $e_I = +0.077$	R = Me: $e_{I^+} = +1.146$
R = Cl: $e_I = +0.089$	R = Cl: $e_{I^+} = +1.153$
R = O <sub>2</sub> N: $e_I = +0.118$	R = O <sub>2</sub> N: $e_{I^+} = +1.165$



**Scheme 3.** Crude estimate of the positive charge on the I-atom of some diaryliodonium ions (MNDO-d; units of electron charge calculated after geometry optimization).

elimination to a less I-(+)-species. Scheme 4 depicts the previously described reaction of 4-nitrophenyl(phenyl)-iodonium triflate with Ph-I to exemplify the latter principle.

The foregoing leads to the prediction that thermal activation of a diaryliodonium triflate such as **1** (or **2**) should result in the formation of an aryl triflate via selective expulsion of the more nucleofugal aryl iodide. Furthermore, the thermal stability of iodane **1** (or **2**) should decrease with increasing I-(+) charge. Experimental support for these predictions is provided by the behavior of iodanes **7–9** (Scheme 5). While **7** was recovered virtually unchanged after heating in DCE solution at 110 °C (careful protection from light, see below), iodane **8**<sup>12</sup> decomposed into mostly 2-iodothiophene, Ph-OTf, and some Ph-I<sup>13</sup> under the same conditions, with a half-life of about 8 h. Variable amounts of a black, insoluble residue (nature unknown) were also formed in the course of such experiments, and the extent of formation of this material increased upon heating **8** to higher temperatures. Under identical conditions, compound **9**<sup>14</sup> degraded completely to such a black material within 5.5 h. Interestingly, thermal degradation occurred faster when **8–9** were heated alone, rather than in the presence of a nucleophilic aryl iodide. This is consistent with the notion that metathesis of **8–9** with an external Ar-I leads to less I-positive, more stable  $\lambda^3$ -iodanes, which therefore decompose more slowly.

Parenthetically, we note that thiophene-based diaryliodonium tetrafluoroborates reportedly suffer from limited shelf life.<sup>15</sup> Yet, properly recrystallized **8–9**, while certainly prone to thermal decomposition, were found to be reasonably stable at (or below) room temperature, so long as they are carefully shielded from light.<sup>16</sup> Noticeable darkening occurred within a few hours upon storage at room temperature in a clear glass container, but wrapping the latter in aluminum foil and keeping it in the dark in a closed cabinet, also at room temperature, preserved the contents intact for at least one month (<sup>1</sup>H NMR). The reported instability may thus be due to inadvertent photodegradation, adventitious contamination, or to an inappropriate choice of counterion (BF<sub>4</sub><sup>(-)</sup> vs. TfO<sup>(-)</sup>).<sup>17</sup>

More significantly, it may be possible to induce metathesis of "unreactive" aryl iodides with iodanes incorporating I-positive aryl iodides such as 2-iodothiophene (Table 1). In keeping with prior art,<sup>1</sup> this surmise was tested by heating a DCE solution of an unreactive aryl iodide and **8** for 12 h in a pressure tube immersed in an oil bath maintained at 110 °C, with careful protection from light. Ligand exchange did occur, albeit at a significantly slower rate relative to the more reactive aryl iodides. A mixture of iodonium triflate products was thus obtained in about 50–60% yield.

The slow reaction rate may be a consequence of not only the diminished I-nucleophilicity of unreactive aryl iodides, but also a more difficult heterolysis of **8**. As seen in Scheme 3, 2-thienyl-

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