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# The electrosynthesis of diaryliodonium salts

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**Abstract**

A simple, one-step procedure for the synthesis of diaryliodonium salts is described. It is shown that the electrochemical oxidation of an aryl iodide at a carbon felt anode in acetic acid/25% acetic anhydride/5% sulfuric acid in the presence of an arene leads to a diaryliodonium salt in good yield. The method allows the preparation of unsymmetrical, as well as symmetrical diaryliodonium salts. © 2000 Elsevier Science Ltd. All rights reserved.

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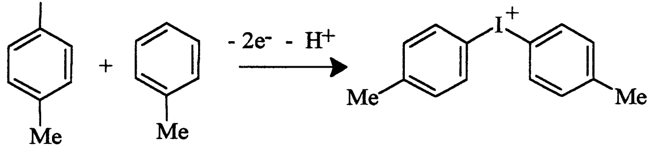
Although polyvalent iodine compounds have been known for some time,[1] there has been a renaissance of interest in their preparation and chemistry since the 1980s.[2–5] They are usually synthesized in a two stage procedure involving the initial oxidation of an aryl iodide followed by acid catalyzed coupling with an arene or activated (silylated) arene. In some cases, the first step may be avoided by using a commercial iodosyl or (diacetoxy)iodo compound with an arene but the number of such reagents is very limited. Alternatively, methods using inorganic iodosyl derivatives have been described but these lead only to symmetrical diaryliodonium salts and can only be used on a small laboratory scale. In principle, anodic oxidation of an aryl iodide in the presence of an arene offers a general and single step approach to the synthesis of diaryliodonium salts and such methods avoid the problems associated with the formation of spent redox reagents. Two papers[6,7] have described the anodic coupling of iodobenzene and benzene to give the diphenyliodonium cation but the electrolyses were carried out in acetonitrile, a solvent widely recognized to be a poor medium for preparative scale oxidations. More recently, two brief conference contributions[8,9] have reported that **1** and **2** could be converted to **3** in high yield by electrolysis at a carbon anode in an undivided cell.



**1** **2** **3**

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The electrolysis medium consisted of a mixture of acetic acid/2% acetic anhydride/5% sulfuric acid. Only very limited experimental information was, however, disclosed. Here, we demonstrate that anodic oxidation in an acetic acid medium is a convenient and general method for the synthesis of diaryliodonium salts and it also allows the preparation of both symmetrical and unsymmetrical diaryliodonium salts.

In an initial set of experiments, the influence of the electrolysis conditions on the selectivity of the reaction was investigated. Table 1 shows the influence of the acetic anhydride content of the medium on the products of electrolyses carried out at a carbon felt anode. It can be seen that with 2% added acetic anhydride, two products, the 4,4′-dimethyldiphenyliodonium cation, **3**, and 4-iodobenzyl acetate, **4**, were always identified. 4-Iodobenzyl acetate is the likely product from the initial attack on the cation radical formed at the anode by nucleophiles/bases, either water or acetic acid; it was also the only major product when the electrolysis of 4-iodotoluene was carried out without toluene in the reaction medium. Increasing the acetic anhydride content of the medium improved the selectivity for the 4,4′-dimethyldiphenyliodonium cation and with 25% acetic anhydride its chemical yield is 92% based on the 4-iodotoluene consumed. At intervals during the electrolysis, samples of the solution were taken and monitored by HPLC. The consumption of both 4-iodotoluene and toluene were linear with charge passed, as was the formation of the 4,4′-dimethyldiphenyliodonium cation. Hence, the selectivity of the reaction does not change with conversion. The influence of current density was also investigated. High yields of the diaryliodonium cation were obtained in acetic acid/25% acetic anhydride/5% sulfuric acid with currents in the range 0.1–0.4 A (equivalent to nominal current densities of 1.25–5 mA cm$^{-2}$ over the surface of the carbon felt anode). In order to obtain a rapid conversion, in all later experiments the cell current was 0.4 A. The current efficiencies for the diaryliodonium cation were, however, only in the range 30–50%. A competing reaction must occur at the anode; since it does not consume the 4-iodotoluene or toluene, it must involve the oxidation of the solvent medium.

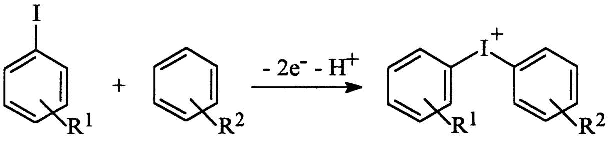
Table 1

Influence on the acetic anhydride content of the electrolysis medium on the products from the electrolysis of 4-iodotoluene (0.2 M) and toluene (0.3 M) at a carbon felt anode in various acetic acid/acetic anhydride mixtures containing 5% $H_2SO_4$

| % $(CH_3CO)_2O$ | Chemical yield/% | |
|---|---|---|
| | **3** | **4** |
| 2 | 46 | 40 |
| 10 | 66 | 23 |
| 25 | 92 | 6 |

The regioselectivity of the coupling was also examined. The coupling of 4-iodotoluene and toluene might be expected to lead to a mixture of 4,4′-dimethylphenyliodonium and 2,4′-dimethylphenyliodonium cations. Indeed, both are formed as can be seen from the $^1$H NMR spectrum. A pure sample of the 2,4′-dimethylphenyliodonium compound was prepared by the electrolysis of 2-iodotoluene and toluene. The ratio of 4,4′-dimethylphenyliodonium to 2,4′-dimethylphenyliodonium cations formed in the electrolysis was estimated from the ratio of the areas under $^1$H NMR peaks at $\delta = 2.30$ and 2.60. The ratio was 9:1, comparable to the selectivity reported from previous electrochemical[8,9] and chemical[10] studies.

The generality of the procedure was examined by the electrolyses of other mixtures of alkyl substituted phenyl iodides and alkylbenzenes in the preferred reaction conditions.



**5** **6** **7**

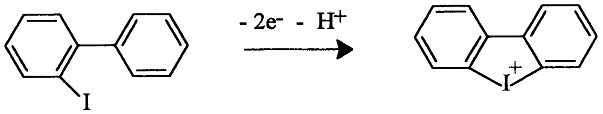
The results are reported in Table 2. It can be seen that the coupling procedure is quite general and unsymmetrical as well as symmetrical, diaryliodonium salts can be formed in good yields. With the larger alkyl substituents, the formation of the 2,4′-derivatives was not apparent from the NMR of the product. This electrochemical procedure is, however, not completely general. For example, when electrolyses were carried out on mixtures of aryl iodides and arenes with electron withdrawing groups, no coupled product was formed. This limitation was also reported previously for the Cr(VI) oxidation[10] of mixtures of aryl iodides and arenes. In addition, not all activated benzenes are stable in the electrolysis medium, e.g. anisole undergoes spontaneous sulfonation within a few minutes.

Table 2

Yields, isolated as iodide salts, and current efficiencies for the formation of diaryliodonium cations **7** by the electrolysis of aryl iodide **5** (0.2 M)+hydrocarbon **6** (0.3 M) at a carbon felt anode in acetic acid/25% acetic anhydride/5% $H_2SO_4$

| $R^1$ | $R^2$ | Product | Yield/% | Current efficiency/% |
|---|---|---|---|---|
| 4-Me | 4-Me | **3** | 92 | 46 |
| 2-Me | 4-Me | **7a** | 77 | 37 |
| 3-Me | 4-Me | **7b** | 83 | 27 |
| 4-Me | 4-Et | **7c** | 71 | 22 |
| 4-Me | 4-*s*-Pr | **7d** | 78 | 22 |
| 4-Me | 4-*t*-Bu | **7e** | 92 | 44 |
| 4-*t*-Bu | 4-Me | **7f** | 48 | 14 |
| 4-*t*-Bu | 4-*t*-Bu | **7g** | 52 | 31 |

On the other hand, intramolecular coupling was possible. Anodic oxidation of 2-iodobiphenyl, **8**, in acetic acid/25% acetic anhydride/5% sulfuric acid led to a 75% yield of the dibenziodonium cation, **9**



**8** **9**

Even in a medium with 2% acetic anhydride, the yield is 60%, reflecting the faster kinetics of intramolecular coupling.

Voltammograms were recorded for a series of aryl iodides and alkylbenzenes at a rotating vitreous carbon disc electrode in the acetic acid/acetic anhydride/sulfuric acid mixture. The aryl iodides all oxidized and gave well formed waves with $E_{1/2}$ in the range +1400 to +1800 mV versus SCE while the aromatic hydrocarbons were oxidized only at more positive potentials very close to those where the electrolysis medium is also oxidised. Therefore, it is confirmed that the coupling reaction results from oxidation of the aryl iodide and the reaction of the resulting cation radical with the aromatic hydrocarbon.

**Experimental**: The electrolysis cell was based on a 250 $cm^3$ beaker. A sheet of carbon felt (dimensions 200×40 mm, thickness 15 mm) was formed into a cylindrical anode around the perimeter of the beaker and a graphite rod cathode was placed at the centre of the beaker so that there was a uniform gap between the two electrodes. The electrolyte was usually 100 $cm^3$ of a solution containing aryl iodide (0.02 mol) and arene (0.03 mol) in acetic acid/25% acetic anhydride/5% sulfuric acid. During the electrolysis, the solution was stirred with a magnetic stirrer bar. A constant current of 0.4 A was passed until a charge equivalent to 1.6 F (80% theoretical charge for the complete conversion of the arene). The consumption of reactants and the formation of product were followed by HPLC. It was possible to isolate the diaryliodonium salts as the bisulfates, white solids being formed on addition of diethyl ether directly to the electrolysis solution. While pure crystals were obtained, the isolated yields were poor. Hence, the products were normally isolated as the iodide salts. At the termination of the electrolyses, the electrodes were washed well with hot methanol and the washings combined with the reaction mixture. The solvents were removed in vacuo and the resulting oil was dissolved in diethyl ether. The dimethyldiphenyliodonium bisulfate was extracted into water and the corresponding iodide was precipitated by the addition of KI. The solid diaryliodonium iodide was dried and weighed (typically 2.5–5 g of the iodide salt was obtained). All products were characterised by $^1H$ and $^{13}C$ NMR and mass spectroscopy.

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