Tetraalkylammonium Dichloroiodates as Iodinating Agents: Absence of Activity in Solid Phases and Superelectrophilic Activity in Sulfuric Acid

Victor D. Filimonov,*[a] Nadya I. Semenischeva,[a] Elena A. Krasnokutskaya,[a] Ho Yun Hwang,[b] Ki-Whan Chi*[b]

[a] Department of Organic Chemistry, Tomsk Polytechnic University, 634050 Tomsk, Russian Federation
Fax +7(3822)563637 ; E-mail: filimonov@tpu.ru

[b] Department of Chemistry, University of Ulsan, 680-749 Ulsan, Korea
E-mail: kwchi@ulsan.ac.kr

Received 14 September 2007; revised 29 October 2007

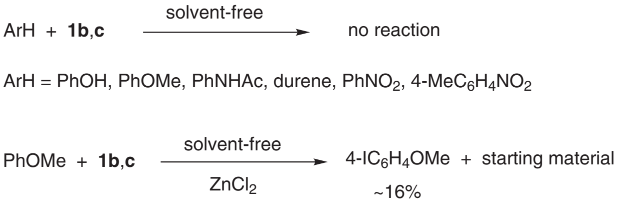
Abstract: In contrast to published results, tetraalkylammonium dichloroiodates ($Alk_4N^+ICl_2^-$) cannot be iodinating reagents for arenes in solvent-free conditions. Nevertheless, tetraalkylammonium dichloroiodates in sulfuric acid solutions or in the presence of Ag_2SO_4 in H_2SO_4 possess superelectrophilic properties and act as very convenient and efficient iodinating agents for deactivated arenes.

Key words: aromatic iodides, tetraalkylammonium dichloroiodates, iodinating agents

Aromatic iodides are indispensable building blocks[1] in organic synthesis and have been independently used as drugs and diagnostic reagents.[2] One of the most widely used iodinating reagents is iodine monochloride.[3] However, it has a number of disadvantages such as strong corrosive characteristics, toxicity, low storage stability, and low iodination selectivity. In 1988, Kajigaeshi et al.[4] developed benzyltrimethylammonium dichloroiodate ($PhCH_2Me_3N^+ICl_2^-$) (**1a**) as an iodinating agent and showed it to be a convenient and effective reagent for the iodination of activated arenes such as alkylbenzenes, phenol ethers, and anilines. The iodination with **1a** was initiated by bases or $ZnCl_2$. Benzyltriethylammonium dichloroiodate ($PhCH_2Et_3N^+ICl_2^-$) was later developed and has similar iodinating reactivity to **1a**.[5] On the other hand, compound **1a** has an intrinsic restriction as iodinating reagent since it cannot iodinate substrates that are less reactive than benzyltrialkylammonium derivatives. More universal and accessible iodinating reagents in this sense may be tetraalkylammonium dichloroiodates, which do not have a benzyl group. To our knowledge, two such reagents are known: tetramethyl- and tetraethylammonium dichloroiodates ($R_4N^+ICl_2^-$) [R = Me (**1b**), R = Et (**1c**)].[5b,6,7] Compounds **1b**,**c** have great potential as iodinating reagents since they are stable and tend to be cheaper than benzyl derivative **1a**. Moreover, they are free from the drawbacks of the parent reagent iodine monochloride. In fact, they could be regarded as a stable and safe alternative for the reactive iodine monochloride.

However, there is little information[5b,7] on their iodinating reactivity and synthetic applicability, and some[6] of the published results are controversial, which will be discussed in this report. In accordance with previous results,[5b,7] salts **1b**,**c** can iodinate only activated arenes in solutions, but the published results of Hajipour et al.[6] are in total contradiction to experimental studies on electrophilic iodination with $R_4N^+ICl_2^-$.[4,5,7] According to Hajipour et al.,[6] a wide range of arenes were iodinated in the solid phase (solvent-free reaction) by simply grinding aromatic substrates in a mortar with **1b** at room temperature, which sharply contradict other experimental data. The authors[6] claim that, under such conditions, deactivated arenes (nitrobenzene, benzoic acid, benzophenone, and others) are also effectively converted into iodoarenes. This indicates that **1b** might be a substantially more reactive reagent than iodine monochloride, which itself could not iodinate nitrobenzene in the solid phase.[8a]

Intrigued by these results, we attempted to reproduce the described iodination procedure.[6] As a result of the repeated experiments in our two labs, no trace of aryl iodides was detected after grinding nitrobenzene or 4-nitrotoluene with **1b**,**c** for 24 hours. On the contrary, it was claimed that the corresponding aryl iodides were provided in 75–82% yield within 45 minutes.[6] Even after the prolonged grinding of activated arenes (phenol, anisole, acetanilide, and durene) with **1b**,**c** only minute quantities of iodine derivatives were identified by TLC, which was also contrary to the results of the paper[6] in that 4-iodoacetanilide and 4-iodoanisole were prepared in 98–100% yield in 5–10 minutes. Moreover, an eight-hour grinding in a mortar with anisole and **1b**,**c** in the presence of $ZnCl_2$, which is known as an iodination activator in solutions,[4d] produced 4-iodoanisole in only 16% yield (Scheme 1). Thus, it is obvious that **1b** and **1c** cannot be iodinating reagents for arenes in a solid-phase reaction contrary to the results of the paper.[6]



Scheme 1 Absence of iodinating reactivity of **1b**,**c** under solvent-free conditions

SYNTHESIS 2008, No. 3, pp 0401–0404
Advanced online publication: 10.01.2008
DOI: 10.1055/s-2008-1032026; Art ID: Z21707SS

It is important to note that there are only a few examples of the iodination of aromatic compounds under solvent-free conditions in solid phase. Besides Hajipour et al.[6] the solid-phase iodination of activated arenes was executed with $I_2/Bi(NO_3)_3$,[9] $I_2/AgNO_3$,[10] ICl, *N*-iodosuccinimide, or $I_2/PhI(OAc)_2$.[8] It is clear that, in general, the main regularities of iodination in the liquid phase appear in the solid phase as well.[8] Hence, our results concerning the inability of **1b**,**c** to iodinate deactivated arenes in the solid phase appear quite as expected.

It is important to note that the above mentioned reactions of the reagent $Me_4N^+ICl_2^-$, obtained both by the method of Hajipour et al.[6] and by the method developed by the authors of this paper (see experimental section), were used. In both cases the two reagents showed low reactivity in solvent-free reactions with aromatic substrates; in addition, they had the same spectral data, but different from the spectral data described by Hajipour et al.[6]

We also have performed calculations of a thermodynamics of iodination of benzene by $Me_4N^+ICl_2^-$ **1b** in the gas phase and in MeOH by using the DFT B3LYP/6-311G* method and Tomasi model (Equation 1). The calculations show that the direct iodination is thermodynamically disfavored both in the gas phase and in solution ($\Delta H_{gas} = 14.83$, $\Delta G_{gas} = 6.37$, $\Delta G_{MeOH} = 20.02$ kcal/mol). Thus, quantum chemical calculations confirm and explain our iodination experiments in solid phase.

$$\mathrm{PhH} + \underset{\mathbf{1b}}{\mathrm{Me_4N^+ICl_2^-}} \rightleftharpoons \mathrm{PhI} + \mathrm{Me_4N^+Cl^-} + \mathrm{HCl}$$

Equation 1

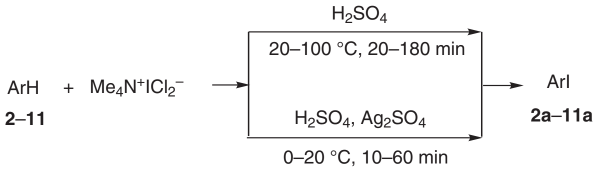
We also have to note that there are a few misunderstandings[11] in the description of properties and spectral data of the iodinated products reported in the paper by Hajipour et al.[6]

Despite these results, we continued our search to extend the applicability of tetraalkylammonium salts as iodinating reagents and found two methods that dramatically increase their electrophilic iodinating reactivity. We found that **1b** in sulfuric acid can effectively iodinate deactivated arenes (Table 1). In this manner, 4-nitroaniline (**2**) is easily iodinated at room temperature within 20 minutes, but for more highly deactivated arenes **3**–**6**, the iodination proceeds at a noticeable speed only at 100 °C to afford the corresponding aryl iodides **3a**–**5a** in high yields. An exception to this is anthraquinone (**6**), which gives 2-iodoanthraquinone (**6a**) in only a 21% yield. As for nitrobenzene, it cannot be iodinated under such conditions (Scheme 2).

Table 1 Iodination of Deactivated Arenes by **1b**,**c** in 93% Sulfuric Acid[a]

Entry	Substrate	Reagent	Time (min)	Temp (°C)	Product	Yield (%)[b]	Mp (°C)
1	4-nitroaniline (**2**)	**1b**	20	20	2-iodo-4-nitroaniline (**2a**)[c]	76	110–111 (110–112)[15]
2	4-nitrotoluene (**3**)	**1b**	50	100	2-iodo-4-nitrotoluene (**3a**)	85	52–54 (52–53)[16]
3	benzoic acid (**4**)	**1b**	60	100	3-iodobenzoic acid (**4a**)	75	184–185 (184–185)[17]
4	**4**	**1b** + Ag_2SO_4	15	20	**4a**[d]	88	184–185 (184–185)[17]
5	benzil (**5**)	**1b**	30	100	3,3′-diiodobenzil (**5a**)	65	127–128 (125–127)[18]
6	**5**	**1b** + Ag_2SO_4	15	0	**5a**[e]	90	127–128 (125–127)[18]
7	anthraquinone (**6**)	**1b**	180	100	2-iodoanthraquinone (**6a**)	21	175–176 (175–176)[19]
8	**6**	**1b** + Ag_2SO_4	180	20	**6a**	73	175–176 (175–176)[19]
9	methyl benzoate (**7**)	**1b** + Ag_2SO_4	15	20	3-iodomenthyl benzoate (**7a**)	96	51–52 (50–52)[20]
10	benzamide (**8**)	**1b** + Ag_2SO_4	15	20	3-iodobenzamide (**8a**)	56	183–184 (183–184)[16]
11	2-iodobenzoic acid (**9**)	**1b** + Ag_2SO_4	60	20	2,5-diiodobenzoic acid (**9a**)	61	180–181 (180.5–181.5)[21]
12	benzaldehyde (**10**)	**1b** + Ag_2SO_4	15	20	3-iodobenzaldehyde (**10a**)	75	55–57 (63–64)[22]
13	nitrobenzene (**11**)	**1b** or **1c**	180	100	3-iodonitrobenzene (**11a**)	traces	35–36 (35–36)[18]
14	**11**	**1b** + Ag_2SO_4	15	20	**11a**	90	35–36 (35–36)[18]
15	**11**	**1c** + Ag_2SO_4	15	20	**11a**	88	35–36 (35–36)[18]

[a] Molar ratio substrate/**1b**,**c** = 1:2; substrate/**1b**,**c**/Ag_2SO_4 = 1:2:2.
[b] Yields of isolated compounds. All products were identified by comparison of melting points with authentic samples.
[c] Molar ratio substrate/**1b** = 1:1.
[d] Molar ratio substrate/**1b**/Ag_2SO_4 = 1:1.5:1.5.
[e] Molar ratio substrate/**1b**/Ag_2SO_4 = 0.5:1.5:1.5.



Scheme 2 Iodination of arenes with **1b** in sulfuric acid

The experimental results show that the iodinating reactivity of **1b** in sulfuric acid was very similar to that of ICl in sulfuric acid,[12] since the reaction time and the yields of the corresponding aryl iodides are comparable with both the reagents. Thus, it can be assumed that in both cases a single-type iodinating intermediate is generated, which is most likely a protonated iodine monochloride ($IClH^+$).

It is also noteworthy that the reactivity of **1b** in sulfuric acid can be significantly increased by adding stoichiometric quantities of silver sulfate. Under these conditions, the iodination of highly deactivated arenes **4–11** proceeds readily at room temperature or even at 0 °C within a short period of time with high yields of the corresponding aryl iodides **4a–11a** (Table 1). In other words, the reagent mixture of **1b**/Ag_2SO_4/H_2SO_4 behaves similarly to superelectrophilic iodinating agents such as *N*-iodosuccinimide in CF_3SO_3H[13a] and H_2SO_4,[13b] 2,4,6,8-tetraiodoglycoluril,[13c] or ICl/Ag_2SO_4[13d] in H_2SO_4. Nearly the same reactivity was observed with **1c**, as shown by the example of nitrobenzene iodination.

On the basis of our previous results[13d] regarding iodination with ICl/Ag_2SO_4 and quantum chemical calculations by DFT,[14] it can be assumed that the main iodinating intermediates in the system with **1b,c**/Ag_2SO_4/H_2SO_4 are the hypoiodite of sulfuric acid ($HOSO_2OI$) and/or its protonated form, $HOSO(OH^+)OI$, which are obtained according to Equation 2.

$$\mathbf{1b,c} + Ag_2SO_4 + H_2SO_4 \longrightarrow 2\,AgCl + HOSO_3I + R_4N^+HSO_4^-$$

Equation 2

In summary, contrary to the results shown by Hajipour et al.,[6] tetramethylammonium dichloroiodate is incapable of iodinating aromatic compounds in the solid phase under solvent-free conditions. This is explained by quantum chemical calculations by DFT. At the same time, we show for the first time that $Alk_4N^+ICl_2^-$ salts in sulfuric acid or in the presence of silver sulfate acquire super-electrophilic ability and are convenient and easily accessible preparative reagents for iodination of deactivated arenes. These results open up a wide range of new opportunities for using tetraalkylammonium dichloroiodates in organic synthesis and enhance the scope of their practical uses.

Column chromatography was performed using silica gel 60, 40–63 μm from Merck. The reaction progress and purity of the obtained products were monitored by TLC, performed on Merck silica gel 60 F_{254} aluminum-backed plates. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-300 spectrometer (^1H NMR, 300 MHz; ^{13}C NMR, 75 MHz) in the indicated solvent. The obtained compounds were identified by comparing their analytic and physicochemical characteristics with those of authentic samples synthesized by conventional methods. All melting points were determined with a Boetius melting point apparatus and are uncorrected.

Tetramethylammonium Dichloroiodate (1b); Typical Procedure

ICl (6.13 g, 38 mmol) that had been mixed beforehand with aq 35% HCl (5 mL) was added to a 64% aq solution of Me_4NCl (6.5 g, 38 mmol). The reaction was immediately followed by the formation of a yellow precipitate, which was then filtered and washed first with a small quantity of H_2O (10 mL) and then with Et_2O (10 mL). The product obtained was dried for 4 h at 50 °C, resulting in the formation of yellow crystals (8.55 g, 83%); mp 206–208 °C (Lit.[6] mp 198–200 °C).

^1H NMR (300 MHz, CD_3CN): $\delta = 3.1$ (s).

^{13}C NMR (75.5 MHz, CD_3CN): $\delta = 54.6$.

Tetraethylammonium Dichloroiodate (1c)

Following the typical procedure for **1b**, compound **1c** was obtained from ICl (6.13 g, 38 mmol) and a 64% aq solution of Et_4NCl (9.81 g, 38 mmol) as a yellow powder; yield: 8.89 g (80%); mp 98–100 °C (Lit.[5b] mp 102–104 °C).

^1H NMR (300 MHz, CD_3CN): $\delta = 1.20$ (t, $J = 7.3$ Hz, 12 H), 3.16 (q, $J = 7.3$ Hz, 8 H).

^{13}C NMR (75.5 MHz, CD_3CN): $\delta = 53.1, 7.6$.

Attempts to Reproduce the Previously Described[6] Procedure for Solvent-Free Iodination of Aromatic Compounds; Solvent-Free Reaction of $Me_4N^+ICl_2^-$ with 4-Nitrotoluene (3)

4-Nitrotoluene (0.27 g, 2 mmol) was added to the iodination reagent **1b** (0.55 g, 2 mmol) in an agate mortar. The mixture was ground with a pestle for 1 min to produce a homogeneous powder, and the mixture was left for 35 min. After that, TLC (benzene) showed only the presence of the starting material (4-nitrotoluene, $R_f = 0.6$). Then, the mixture was again left for 14 h and aq 10% Na_2SO_3 (15 mL) was added. The mixture was extracted with Et_2O (3 × 10 mL) and the combined Et_2O layers were dried ($MgSO_4$), and evaporated to obtain the unreacted 4-nitrotoluene (**3**; 0.26 g, 95%); mp 51–52 °C (Lit.[15] 52–54 °C).

Solvent-Free Reaction of $Me_4N^+ICl_2^-$ with Acetanilide

Acetanilide (0.27 g, 2 mmol) was added to the iodination reagent **1b** (0.55 g, 2 mmol) in an agate mortar. The mixture was ground with a pestle for 1 min to produce a homogeneous powder, and the mixture was left for the 10 min. After that, TLC (benzene–EtOH, 8:2) showed only the presence of the starting material ($R_f = 0.6$). Then, the mixture was left for 14 h and aq 10% Na_2SO_3 (15 mL) was added. The mixture was extracted with Et_2O (3 × 10 mL) and the combined Et_2O layers were dried ($MgSO_4$). Evaporation of the solvent afforded white crystals of unreacted acetanilide (0.25 g, 93%); mp 113–115 °C (Lit.[15] 113–115 °C).

Iodination of Arenes by Reagents 1b,c; General Procedure

To 93% H_2SO_4 (15 mL) at 5–7 °C was added the reagent **1b** or **1c** (3.6 mmol) in small portions followed by an aromatic substrate (3 mmol). The mixture was stirred for the time and at the temperature indicated in Table 1. The mixture was poured into H_2O (100 mL) followed by the addition of aq 10% Na_2SO_3 (15–20 mL). The precipitate was either collected by filtration, or extracted with $CHCl_3$ (2 × 30 mL) and worked up in the usual way by evaporating the solvent.

Iodination of Arenes by Reagents 1b,c in the Presence of Ag_2SO_4; General Procedure

Ag_2SO_4 (1.9 g, 6 mmol) was dissolved in a 93% H_2SO_4 (15 mL). Small portions of the reagent **1b** or **1c** (6 mmol) were added to the solution at 5–7 °C. The precipitated AgCl was filtered off. An aromatic substrate (3 mmol) was added to the resulting dark-brown solution of the iodinating reagent. The reaction was allowed to proceed with stirring for the time indicated in Table 1. Isolation of iodine derivatives was carried out under the above mentioned procedure for the iodination of arenes by the reagents **1b**,**c**.

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(11) (a) For example, the NMR spectra for 4-iodoanisole given in the paper[6] differ sharply from those published in other papers (see ref.[11b]) – there are only six ^{13}C signals instead of five, and carbons are missing at appropriate shifts to be next to iodine and OCH_3 group ($\delta = 82.5$ and 159.4). In the ^{13}C NMR spectrum[6] of 3-iodo-4-methoxybenzyl alcohol there are no C_{aryl}–I and C_{aryl}–OCH_3 ($\delta = 89$ and 156) signals as well. The reported melting point (mp 142–144 °C) of 3-iodo-4-methoxybenzyl alcohol indicated in the paper[6] is totally different from those previously published (mp 84 °C,[11c] mp 81–82 °C[11d]), and similar inconsistence is observed for 4-iodo-1,2-dimethoxybenzene (mp 77–78 °C,[6] mp 33 °C,[11e] mp 33–34 °C[4b]). The authors of the paper[6] refer to the reference 5b in order to confirm the melting point (mp 142–144 °C), but this paper[5b] does not have any data on this compound. In the ^{13}C NMR spectrum for 3-(3-iodo-4-aminophenyl)propionic acid in the paper,[6] the chemical shift for C_{aryl}–I ($\delta = 80$–90) is absent. The MS data for *m*-iodococaine indicated in the paper[6] are in sharp contradiction with the previously published data.[11f] (b) dos Santos, M. L.; de Magalhaes, G. C.; Filho Braz, R. *J. Organomet. Chem.* **1996**, *526*, 15. (c) Gaux, B.; le Henaff, P. *Bull. Soc. Chim. Fr.* **1974**, 505. (d) Pavlinac, J.; Zupan, M.; Stavber, S. *J. Org. Chem.* **2006**, *71*, 1027. (e) Seer, K. *Monatsh. Chem.* **1913**, *34*, 631. (f) Yu, D. W.; Gatley, S. J.; Wolf, A. P.; MacGregor, R. R.; Dewey, S. L.; Fowler, J. S.; Schlyer, D. J. *J. Med. Chem.* **1992**, *35*, 2178.

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