Bull. Chem. Soc. Jpn., 72, 115—120 (1999)

Oxidative Iodination of Arenes with Manganese(IV) Oxide or Potassium Permanganate as the Oxidants

Piotr Luliński and Lech Skulski*

Chair and Laboratory of Organic Chemistry, Medical Academy, Banacha 1, PL 02-097 Warsaw, Poland

(Received September 16, 1998)

Novel and easy laboratory methods (novel Procedures **1**—**4**) are presented for the oxidative mono- and diiodination of both *activated* and *deactivated* arenes, which gave the pure iodinated products in 62—89% yields. The reactions were carried out in the *anhydrous*, strongly acidic system, I_2/activated MnO_2/AcOH/Ac_2O/concd H_2SO_4, firstly at r.t. for 2 h, then at 45—55 °C for 2—9 h. The resulting mixtures were poured into excess aq Na_2SO_3 solution buffered with $(NH_4)_2CO_3$ to neutralize H_2SO_4. The following workups are given. Similarly, on carrying out the iodination reactions (at 35 °C, for one hour) in the *anhydrous*, strongly acidic system, I_2/$KMnO_4$/AcOH/Ac_2O/concd H_2SO_4, it was possible to mono- or diiodinate several *deactivated* arenes in 73—87% yields (improved Procedures **5** and **6**).

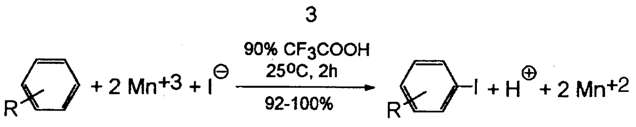
Aromatic iodides are widely used in organic synthesis, hence many different methods, and their improvements, have been reported for their effective preparation.[1] In two former papers[2,3] we reported simple and efficient laboratory methods: either for iodination of some highly activated arenes with molecular iodine (diiodine) in the presence of lead(IV) acetate in glacial acetic acid,[2] or for iodination of both activated and deactivated arenes in the *anhydrous*, strongly acidic liquid system, I_2/CrO_3/AcOH/Ac_2O/concd H_2SO_4.[3]

In the present paper we report ***novel***, simple laboratory methods for mono- and diiodination of both *activated* and *deactivated* arenes in the *anhydrous*, strongly acidic system, I_2/activated MnO_2/AcOH/Ac_2O/concd H_2SO_4 (novel Procedures **1**—**4**) as well as ***improved*** laboratory methods for mono- and diiodination of some *deactivated* arenes in the *anhydrous*, strongly acidic system, I_2/$KMnO_4$/AcOH/Ac_2O/concd H_2SO_4 (improved Procedures **5** and **6**). Both activated MnO_2[4,5] and $KMnO_4$[4] are common and easily handled oxidants, and their applications in organic synthesis have been known for a long time. To our knowledge,[6,7] Mn(II) salts left in the residues after the iodination reactions are less toxic as compared with Pb(II) or Cr(III) salts, being the side-products in our former iodination procedures.[2,3]

So far, no one has applied *manganese(IV)* oxide as the oxidizing reagent used in *stoichiometric quantities* in the aromatic iodination reactions. Japanese chemists[8] iodinated benzene with diiodine, in pressurized air or oxygen gas, in acidic solvents, using twenty four metal salts or oxides as *catalysts*; they also mentioned there *a manganese(IV)* oxide and added that Cu, Ti, Fe, and Mn salts were comparatively effective. The iodination rate depended on the acidity of solvent applied: $CF_3SO_3H > CH_3SO_3H > CF_3COOH \gg CH_3COOH$. Iodobenzene was obtained in excellent yield (91.9%) when $NaVO_3$ and CF_3SO_3H were used. According to them, the combination of strong acidic solvent, oxygen gas, and oxidizing catalyst are indispensable in the iodination reaction, whereas the sort of counter ions of metal ions do not seem to be important. Later, the last statement was experimentally denied by Soviet authors,[9] who applied four various chromium(VI) salts used in stoichiometric quantities for the aromatic iodination of benzene and toluene, and qualitatively arranged the oxidizing activity of the dichromates as follows: $K_2Cr_2O_7 < Na_2Cr_2O_7 < Li_2Cr_2O_7 < (NH_4)_2Cr_2O_7$, used under the same reaction conditions. A similar arrangement would propably exist also for various metal manganates or permanganates.

The oxidative iodination of benzenes having no strong electron-donating or electron-withdrawing substituents was accomplished by another group of Soviet chemists[10] with stoichiometric quantities of *manganese(III) acetate* [as well as with cobalt(III) acetate and cerium(IV) sulfate, for the sake of comparison] in 90% CF_3COOH (Scheme 1):

According to Merkushev,[1] the obvious synthetic advantages of this method are as follows: the possibility of replacement of elemental iodine, usually requiring purification and careful grinding before use, by readily accessible alkali iodides of high purity (previously dissolved in a little **water**), which are completely spent in the reaction; the reaction does not require heating or use of expensive and toxic oxidants. Reduced form of metal and CF_3COOH could be readily re-



R = H, 4-CH3, 4-F, 4-Cl, 4-Br, 4-I
(the products were admixtured with *ortho*-substituted isomers).

Scheme 1.

generated. In most cases, near quantitative yields of aryl iodides, ArI, were obtained.

Chaikovskii and Novikov[11] oxidatively iodinated benzene, its various derivatives, and some aromatic hydrocarbons, using stoichiometric quantities of *potassium permanganate* as the oxidant. They worked up two simple procedures, carrying out the iodination reactions (at 100—115 °C, within 1—5 h) in the following systems: *Procedure 1*: $I_2/KMnO_4$/glacial AcOH/concd H_2SO_4 or *Procedure 2*: $I_2/KMnO_4$/80% AcOH/concd H_2SO_4. Generally, the corresponding mono- and diiodinated products were obtained in 26—99% yields. In the *Procedure 1* they used a *commercial* glacial acetic acid—probably containing an admixture of **water** which, due to its high hydration power, diminishes the oxidizing activity of inorganic oxidants. Hence, on iodinating benzoic acid and 9,10-phenanthrenequinone they obtained the corresponding iodinated products in moderate yields: 3-iodobenzoic acid (49%) and 2,7-diiodo-9,10-phenanthrenequinone (35%). We considerably **improved** the said Soviet *Procedure 1*, suitable for iodination of deactivated arenes, carrying out the iodination reactions in the *anhydrous*, strongly acidic system, $I_2/KMnO_4/AcOH/Ac_2O$/concd H_2SO_4, with lowering the reaction temperature to 35 °C, and shortening the reaction time to one hour (see our improved Procedures **5** and **6** submitted in Experimental, and the Table 1). It is seen there that our iodination yields are considerably higher: 3-iodobenzoic acid (78%) and 2,7-diiodo-9,10-phenanthrenequinone (85%). The same is true in respect to the iodination of other deactivated benzenes: methyl 3-iodobenzoate (83%), ethyl 3-iodobenzoate (73%), and 3,3′-

Table 1. Iodinated Pure Products Prepared (Checked with TLC)

Substrate	Procedure	Product	Yield %	Analysis/I_2% Calcd (Found)	Mp/°C/solvent[a] (lit)[18]
C_6H_6	**1**	PhI	63	62.23 (62.03)	bp 78—80/25 (bp 63—64/8; 188/760)
C_6H_6	**2**	1,4-$C_6H_4I_2$	66	76.95 (76.77)	129—131/**B**,**E** (129)
PhI	**1**	1,4-$C_6H_4I_2$	70	76.95 (76.73)	129—131/**B**,**E** (129)
PhBr	**1**	1,4-C_6H_4BrI	77	44.87 (44.78)	89—91/**H**,**E** (91—92)
PhCl	**1**	1,4-C_6H_4ClI	68	53.22 (52.62)	56—57/**E**,**I** (57)
PhF	**1**	1,4-C_6H_4FI	71	57.18 (57.33)	bp 68—70/16 (bp 182—184/760)
PhMe	**1**	1,4-MeC_6H_4I[b]	62	58.22 (57.54)	bp 84—88/15 (bp 100/25; 36—37)
PhCOOH	**3**	1,3-IC_6H_4COOH	87	51.17 (51.08)	186—187/**C**,**D** (187—188)
PhCOOH	**5**	1,3-IC_6H_4COOH	78	51.17 (50.56)	190—191/**C**,**D** (187—188)
PhCOOMe	**3**	1,3-IC_6H_4COOMe	89	48.43 (48.02)	52—54/**P** (54—55)
PhCOOMe	**5**	1,3-IC_6H_4COOMe	83	48.43 (48.36)	52—54/**P** (54—55)
PhCOOEt	**3**	1,3-IC_6H_4COOEt	79	45.97 (45.70)	bp 154—156/28 (bp 150.5/15)
PhCOOEt	**5**	1,3-IC_6H_4COOEt	73	45.97 (46.01)	bp 160—161/38 (bp 150.5/15)
PhCOPh	**4**	3-$IC_6H_4COC_6H_4I$-3′	78	58.48 (58.38)	147—149/**B**,**A** (152.5—153.5)
PhCOPh	**6**	3-$IC_6H_4COC_6H_4I$-3′	87	58.48 (58.31)	141—142/**B**,**A** (152.5—153.5)
$PhCONH_2$	**3**	1,3-$IC_6H_4CONH_2$	63	51.37 (51.32)	186—187/**E** (186.5)
$PhNO_2$	**3**	1,3-$IC_6H_4NO_2$	73	50.96 (50.57)	37—38/**P** (bp 153/14; 38)
9,10-Phenanthrenequinone	**4**	2,7-Diiodo-9,10-phenanthrenequinone	72	55.17 (53.81)	326—328/**Z** (310)[19]
9,10-Phenanthrenequinone	**6**	2,7-Diiodo-9,10-phenanthrenequinone	85	55.17 (53.56)	319—321/**Z** (310)[19]

[a] Solvents used for crystallization: **A**, Me_2CO; **B**, *t*-butyl alcohol; **C**, $CHCl_3$; **D**, CCl_4; **E**, EtOH; **H**, hexane; **I**, isopropyl alcohol; **P**, petroleum ether; **Z**, chlorobenzene. [b] There is a mixture of *o*- and *p*-isomers (ratio 1 : 5; ^1H NMR). Haloiodobenzenes were not investigated with ^1H NMR; cf. Ref. 10.

diiodobenzophenone (87%). However, we failed to iodinate *nitrobenzene* with our improved Procedure **5**—which was also not reported by the Soviet chemists.[11)]

Finally, Chinese chemists from Taiwan[12)] iodinated various arylamines with a homogeneous mixture of hydroiodic acid and *potassium permanganate* in acetonitrile. *para*-Substituted products were obtained in high yields (71—78%) within twelve hours at room temperature. With a slight modification of the $KMnO_4 : HI :$ substrate ratio, iodination of alkynes to *vic*-diiodoalkenes could be carried out at 60 °C in 65—87% yields. This reagent is highly selective for arylamines, but *unsuitable* for phenols, which undergo oxidative coupling easily in the presence of electron transfer agent; see this paper for more details and references.

Results and Discussion

In this work, the particular emphasis was put on developing the effective iodination procedures for *deactivated* arenes, since there is a number of simple, and environmentally safe, methods for iodination of activated arenes;[1)] cf. also our former work.[3)]

Starting our experiments with *manganese(IV) oxide*, we checked experimentally various brands of this oxidant. Ordinary commercial MnO_2 was not applicable. The best iodination yields (Table 1) were obtained with the *activated* MnO_2 freshly prepared[13)] prior to use. An activated commercial product (Aldrich–Sigma) gave the yields by ca. 5—10% lower.

For benzene, toluene, and four halobenzenes, the iodination reactions were carried out according to the following stoichiometry (novel Procedure **1**):

$$2\text{Ar–H} + I_2 + MnO_2 + 2Ac_2O + H_2SO_4 \xrightarrow[\text{AcOH/Ac}_2\text{O}]{\substack{\text{1) r.t., 2 h}\\ \text{2) 45—55 °C, 2 h}}} 2\textbf{Ar-I} + MnSO_4 + 4AcOH \qquad (1)$$

Presumably, transient *iodine(I)* species were preponderantly acting there (as weaker electrophiles) upon the six reacted arenes. We have also observed that after one suspends MnO_2 and diiodine in a cooled (5 °C) mixture of acetic acid with acetic anhydride, the following concentrated (98%) H_2SO_4 should be added dropwise very slowly to keep the temperature **below 10 °C** (strongly exothermic reaction). Next, the said arenes were added, and the reaction mixtures were stirred at room temperature for 2 h,[14)] then for two subsequent hours at 45—55 °C (the main iodination reaction). Finally, the reactions were quenched by pouring the resulting reaction mixtures into excess aqueous Na_2SO_3 solution buffered with $(NH_4)_2CO_3$ to neutralize H_2SO_4. The solid or oily products were separated and purified by common laboratory techniques (Experimental), which resulted in 62—77% yields of the monoiodinated products (Table 1).

Similarly, with our novel Procedure **2** we obtained 1,4-diiodobenzene (66%) from benzene according to a changed stoichiometry:

$$C_6H_6 + I_2 + MnO_2 + 2Ac_2O + H_2SO_4 \xrightarrow[\text{AcOH/Ac}_2\text{O}]{\substack{\text{1) r.t., 2 h}\\ \text{2) 45—55 °C, 2 h}}} \mathbf{1,4\text{-}C_6H_4I_2} + MnSO_4 + 4ArOH \qquad (2)$$

For the oxidative iodination of *deactivated* arenes, the stronger electrophiles, i.e. transient *iodine(III)* species, are indispensable to attain possibly highest iodination yields. Hence, we changed the general reaction stoichiometry as follows (novel Procedure **3**):

$$2\text{Ar–H} + I_2 + 3MnO_2 + 6Ac_2O + 5H_2SO_4 \xrightarrow[\text{AcOH/Ac}_2\text{O}]{\substack{\text{1) r.t., 2 h}\\ \text{2) 45—55 °C, 2—9 h}}} 2\text{Ar–ISO}_4 + 3MnSO_4 + 12AcOH \qquad (3)$$

which would strongly favor the formation of transient *iodine(III)* species. By pouring the resulting reaction mixtures into excess aqueous Na_2SO_3 solution (see Eq. 4) buffered with $(NH_4)_2CO_3$, we obtained—after the separation and purification of the crude products (Experimental)—the five monoiodinated *deactivated* arenes in 63—89% yields, including 3-iodonitrobenzene (73%) (Table 1).

It is known from previous works[1,3,15)] that in the *anhydrous*, strongly acidic media, such the strong oxidants as CrO_3 or $KMnO_4$ (in excess) may oxidize elemental iodine to some transient *iodine(III)* species, acting upon deactivated or activated arenes as stronger electrophiles than transient *iodine(I)* species. We have observed in our numerous experiments that in the presence of **water** the assumed transient *iodine(III)* species are unstable, and propably very quickly deteriorate to form less reactive and more stable *iodine(I)* species. Hence, the *anhydrous* and strong acidic conditions are recommended to attain the highest yields of the assumed organic *iodine(III)* intermediates, Ar–ISO_4 or Ar–$I(OSO_3H)_2$, derived from the reacted arenes.[3,16)] After completing the iodination reactions, the reaction mixtures were poured into excess aqueous Na_2SO_3 solution [which also destroyed unreacted diiodine and other possible oxidizing contaminants, e.g. Mn(IV) and Mn(III) species] buffered with varied amounts of $(NH_4)_2CO_3$ to neutralize all H_2SO_4:

$$2\text{Ar–ISO}_4 + 2Na_2SO_3 + 2H_2O \xrightarrow{\text{quick reaction}} 2\textbf{Ar-I} + 2Na_2SO_4 + 2H_2SO_4 \qquad (4)$$

In our novel Procedure **4** (Experimental) we halved the amounts of *deactivated* arenes added to the reaction mixtures to obtain the respective diiodinated products, viz. 3, 3′-diiodobenzophenone (78%), and 2,7-diiodo-9,10-phenanthrenequinone (72%).

The stoichiometry obeyed in our improved Procedure **5** (Experimental), which strongly favors the formation of transient *iodine(III)* species, is as follows:

$$2\text{Ar–H} + I_2 + 1.2KMnO_4 + 4.8Ac_2O + 3.8H_2SO_4 \xrightarrow[\text{AcOH/Ac}_2\text{O}]{\text{35 °C, 1 h}} 2\text{Ar–ISO}_4 + 1.2MnSO_4 + 0.6K_2SO_4 + 9.6AcOH \qquad (5)$$

After pouring the reaction mixtures into excess aqueous

Na_2SO_3 solution (see Eq. 4) buffered with $(NH_4)_2CO_3$, and the separation and purification of the crude products (Experimental), the three monoiodinated deactivated arenes were obtained in 73—78% yields (Table 1).

In our improved Procedure **6** (Experimental) we halved the amounts of deactivated arenes added to the reaction mixtures to obtain the respective diiodinated products, viz. 3,3′-diiodobenzophenone (87%) and 2,7-diiodo-9,10-phenanthrenequinone (85%).

Summing up, our novel Procedures **1—4** and improved Procedures **5** and **6** presented in this paper, gave the purified mono- or diiodinated products in good or excellent 62—89% yields. In our opinion, particularly interesting are the iodination results obtained with the *deactivated* arenes.

The structures of the purified iodinated products (their purity was also checked by TLC), all known in the literature, were supported by their melting points (or boiling points) compared with those submitted in the literature (Table 1) as well as with mixed melting points with authentic specimens.[2,3] The structures were also corroborated by elemental analyses (Table 1).

Experimental

Melting or boiling points in the Table 1 are uncorrected. The commercial reagents and solvents were purified or dried, if necessary, prior to use. Molecular iodine (diiodine), $KMnO_4$, and *activated* MnO_2 should be ***finely powdered*** in order to facilitate their dissolution. *Activated* MnO_2 was prepared according to the literature procedure;[13] a commercial product (Aldrich–Sigma) also was applied for the sake of comparison. Elemental analyses were carried out at the Institute of Organic Chemistry, the Polish Academy of Sciences, Warsaw.

The *toxic* residues containing Mn(II) salts were collected and disposed of according to the local safety measures. Working in the laboratory scale, we did not remove or recover cheap manganese salts from the residues.

Procedure 1: The Monoiodination of Some More Active Arenes with Activated MnO_2 as Oxidant: Activated MnO_2 (2.17 g, 25.0 mmol; 25% excess established to be the most appropriate) and diiodine (5.08 g, 20.0 mmol; 0% excess) were suspended in a stirred mixture of glacial AcOH (30 ml) with Ac_2O (15 ml) cooled to 5—10 °C. Alternatively, *varied quantities*[17] (see below) of concentrated (98%) H_2SO_4 were very slowly added dropwise, with vigorous stirring and keeping the temperature at 5—10 °C (*strongly exothermic reaction*), viz.

(a) for toluene, 4.80 ml (8.83 g; 90 mmol) of concd H_2SO_4 was added;

(b) for benzene, fluorobenzene, and bromobenzene, 9.59 ml (17.7 g; 180 mmol) of concd H_2SO_4 was added;

(c) for chlorobenzene, 10.7 ml (19.6 g; 200 mmol) of concd H_2SO_4 was added;

(d) for iodobenzene, 13.3 ml (24.6 g; 250 mmol) of concd H_2SO_4 was added.

An appropriate *arene* (44.0 mmol; 10% excess) was added portionwise or dropwise with stirring, and the stirring was continued for 2 h at room temperature.[14] Then the reaction mixture was heated under reflux, with stirring, at 45—55 °C for 2 h. The mixture was left overnight at room temperature. The reaction mixture was poured, as above, into ice-water containing the previously dissolved Na_2SO_3 (6.3 g, 50 mmol in Procedures **1** and **2**; 12.6 g, 100 mmol in Procedures **3—6**) and varied amounts of $(NH_4)_2CO_3$ to neutralize all H_2SO_4 (*foaming*). After ca. 30 min, the *solid* products were collected by filtration, washed well with water until the washing were colorless and neutral, air-dried, and recrystallized from appropriate solvents (Table 1). The *oily* products were extracted with $CHCl_3$ (3×30 ml), the collected extracts were dried ($MgSO_4$), the solvent was distilled off, and the residues were fractionated under vacuum (Table 1).

Procedure 2: The Diiodination of Benzene with Activated MnO_2 as Oxidant: Activated MnO_2 (2.17 g, 25.0 mmol; 25% excess) and diiodine (5.58 g, 22.0 mmol; 10% excess) were suspended in a mixture of glacial AcOH (30 ml) with Ac_2O (15 ml) cooled to 5—10 °C. Concentrated (98%) H_2SO_4 (14.4 ml, 26.5 g; 270 mmol) was very slowly added dropwise, with vigorous stirring and keeping the temperature at 5—10 °C (*strongly exothermic reaction*), then followed with *benzene* (1.77 ml, 20.0 mmol; 0% excess) at room temperature, and the stirring was continued for 2 h at room temperature.[14] Then, the whole was stirred under reflux for 2 h at 45—55 °C; after ca. 1 h, a thick slurry was formed. This was left overnight at room temperature. The reaction mixture was poured, as above, into ice-water containing prior dissolved Na_2SO_3 and $(NH_4)_2CO_3$ (*foaming*). After ca. 30 min, the collected precipitate was worked up as above in Procedure **1** (Table 1).

Procedure 3: The Monoiodination of Some Deactivated Arenes with Activated MnO_2 as Oxidant: Activated MnO_2 (2.87 g, 33.0 mmol; 10% excess) and diiodine (2.79 g, 11.0 mmol; 10% excess) were suspended in a stirred mixture of glacial AcOH (30 ml) with Ac_2O (15 ml) cooled to 5—10 °C. Alternatively, *varied quantities*[17] (see below) of concentrated (98%) H_2SO_4 were very slowly added dropwise, with vigorous stirring and keeping the temperature at 5—10 °C (*strongly exothermic reaction*), viz.

(a) for benzoic acid and its ethyl and methyl esters, 10.7 ml (19.6 g; 200 mmol) of concd H_2SO_4 was added;

(b) for benzamide, 12.8 ml (23.5 g; 240 mmol) of concd H_2SO_4 was added;

(c) for nitrobenzene, 48.0 ml (88.3 g; 900 mmol) of concd H_2SO_4 was added; when only 32.0 ml (600 mmol) of concd H_2SO_4 was added, the 3-iodonitrobenzene was obtained in 63% yield.

An appropriate deactivated *arene* (20.0 mmol; 0% excess) was added at room temperature, and the stirring was continued for 2 h at room temperature.[14] Then, the whole was stirred under reflux at 45—55 °C for 2 h [for ethyl and methyl benzoates for 5 h; for nitrobenzene for 9 h]. The mixture was left overnight at room temperature. The reaction mixture was poured as above into ice-water containing the previously dissolved Na_2SO_3 and $(NH_4)_2CO_3$ (*foaming*). After ca. 30 min, the collected precipitates were worked up as above in Procedure **1** (Table 1).

When *benzene* was iodinated with Procedure **3**, the yield of iodobenzene was negligible. However, from the collected aqueous layers we precipitated out a *yellow solid* with excess aq KI. This was collected by filtration, washed with water, and *quickly* recrystallized from MeOH. We obtained pure **diphenyliodonium iodide** (43%), mp 168—169 °C (decomp), lit,[15] mp 166—167 °C (decomp). Its structure was supported with mixed mp and ^{1}H NMR spectrum (in DMSO-d_6) as being identical to that reported in Ref. 15. See also our former work,[3] pp. 1669—1670.

Erratum. In our former work[3] we precipitated out, in fact, **diphenyliodonium bromide** (44%) *with excess aq KBr*. The mp given there for the purified product is correct, as well as all the following information.

Procedure 4: The Diiodination of Benzophenone or 9,10-Phenanthrenequinone with Activated MnO_2 as Oxidant: Activated MnO_2 (2.87 g, 33.0 mmol; 10% excess) and powdered I_2 (2.79 g, 11.0 mmol; 10% excess) were suspended in a stirred mixture of glacial AcOH (20 ml) with Ac_2O (10 ml) cooled to 5—10 °C. Concentrated (98%) H_2SO_4 (12.8 ml, 23.5 g; 240 mmol) was very slowly added dropwise, with vigorous stirring and keeping the temperature at 5—10 °C (*strongly exothermic reaction*). An appropriate deactivated *arene* (10.0 mmol; 0% excess) was added, and the stirring at room temperature was continued for 2 h.[14] Then, the whole was stirred under reflux at 45—55 °C for 2 h, and left overnight at room temperature. The reaction mixture was poured, as above, into ice-water containing the previously dissolved Na_2SO_3 and $(NH_4)_2CO_3$ (*foaming*). After ca. 30 min, the collected precipitates were worked up as above in Procedure **1** (Table 1).

Procedure 5: The Improved Monoiodination of Some Deactivated Arenes with $KMnO_4$ as Oxidant; cf. Ref. 11. Powdered $KMnO_4$ (5.45 g, 34.5 mmol; 15% excess established to be the most appropriate) was suspended in a mixture of glacial AcOH (50 ml) with Ac_2O (30 ml) cooled to 5—10 °C. Diiodine (7.30 g, 28.8 mmol; 15% excess) was added, and concentrated (98%) H_2SO_4 (16.0 ml, 29.4 g; 300 mmol) was slowly added dropwise with stirring and keeping the temperature below 10 °C. An appropriate *arene* (50.0 mmol; 0% excess) was added, and the whole was stirred for 1 h at 35 °C. The reaction mixture was poured, with stirring, into ice-water (200 ml) containing the previously dissolved Na_2SO_3 and $(NH_4)_2CO_3$ (*foaming*). After ca. 30 min, the collected precipitates were worked up as above in Procedure **1** (Table 1).

Procedure 6: The Improved Diiodination of Some Deactivated Arenes with $KMnO_4$ as Oxidant; cf. Ref. 11. A mixture of powdered $KMnO_4$ (5.45 g, 34.5 mmol; 15% excess), diiodine (7.30 g, 28.8 mmol; 15% excess), glacial AcOH (50 ml), and Ac_2O (30 ml) was prepared as above, and cooled to 5—10 °C. Concentrated (98%) H_2SO_4 (20.0 ml, 36.8 g; 375 mmol) was slowly added dropwise with stirring and keeping the temperature below 10 °C. An appropriate *arene* (25.0 mmol; 0% excess) was added, and the mixture was stirred for 1 h at 35 °C. The reaction mixture was poured, as above, into ice-water containing the previously dissolved Na_2SO_3 and $(NH_4)_2CO_3$ (*foaming*). After ca. 30 min, the collected precipitates were worked up as above in Procedure **1** (Table 1).

In the above Procedures **2**—**6**, the yields of the mono- and diiodinated products given in the Table 1 were calculated from the total amounts of the ***arenes*** used in the reactions, whereas in Procedure **1** they were calculated from the total amounts of the ***diiodine*** used in the reactions.

These results were presented at the IVth All-Polish Symposium on the Organic Chemistry, Łódź (Poland), January 22—24, 1997. They are a part of the future dissertation of P. Luliński, M. Sc.

References

1) The newest reviews on aromatic iodination: a) E. B. Merkushev, *Synthesis*, **1988**, 923; b) Y. Sasson, "Formation of Carbon–Halogen Bonds (CI, Br, I)," in "The Chemistry of Halides, Pseudo-Halides, and Azides, Supplement D1," ed by S. Patai and Z. Rappoport, Wiley-Interscience, Chichester (1995), pp. 535—620; c) P. G. Steel, "Halobenzenes," in "Rodd's Chem. Carbon Compds.," 2nd ed, ed by M. Sainsburry, Elsevier, Amsterdam (1996), Vol. 3, Part 1, pp. 178—224; d) P. L. Spargo, *Contemp. Org. Synth.*, **1**, 113 (1994); e) P. L. Spargo, *Contemp. Org. Synth.*, **2**, 85 (1995); f) S. P. Marsden, *Contemp. Org. Synth.*, **3**, 133 (1996); g) S. P. Marsden, *Contemp. Org. Synth.*, **4**, 118 (1997); h) S. D. R. Christie, *J. Chem. Soc., Perkin Trans. 1*, **1998**, 1577.

2) B. Krassowska-Świebocka, P. Luliński, and L. Skulski, *Synthesis*, **1995**, 926. In its Refs. 1, 2, 3, and 4 there is a list of the former reviews and papers dealing with the aromatic iodination.

3) P. Luliński and L. Skulski, *Bull. Chem. Soc. Jpn.*, **70**, 1665 (1997).

4) a) L. F. Fieser and M. Fieser, "Reagents in Organic Synthesis," Wiley-Interscience, New York– London– Sydney, Vols. 1—12; Russian transl. "Reagenty dlya organicheskogo sinteza," Vols. 1—7, Izd. Mir, Moscow (1970—1978); b) "Oxidation in Organic Chemistry," ed by K. W. Wiberg, Academic Press, New York– London (1965); c) "Oxidation. Techniques and Application in Organic Synthesis," ed by R. L. Augustine, M. Dekker, New York (1969).

5) A. J. Fatiadi, *Synthesis*, **1976**, 65 and 133 (Parts I and II).

6) N. V. Lazarev, "Khimicheski vrednye veshchestva v promyshlennosti," Goskhimizdat, Leningrad– Moscow (1951); Polish transl., "Szkodliwe substancje w przemyśle," Państw. Wydawn. Techn., Warsaw (1956).

7) W. Czerska, M. J. Malawski, and J. Surowiński, "Vademecum drogisty. Substancje nieorganiczne," Vol. I, Biuro Wyd. CHPCh "Chemia," Wyd. Katalogów i Cenników, Warsaw (1966).

8) A. Shimizu, K. Yamataka, and T. Isoya, *Bull. Chem. Soc. Jpn.*, **58**, 1611 (1985).

9) M. G. Grigor'ev, I. A. Buketova, and P. F. Polevshchikov, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **30**, 22 (1987); *Chem. Abstr.*, **109**, 6142 (1988).

10) D. I. Makhon'kov, A. V. Cheprakov, M. A. Rodkin, and I. P. Beletskaya, *Zh. Org. Khim.*, **22**, 1117 (1986); *J. Org. Chem. USSR*, **22**, 1001 (1986).

11) V. K. Chaikovskii and A. N. Novikov, *Zh. Prikl. Khim.*, **57**, 134 (1984); *Chem. Abstr.*, **100**, 191452 (1984).

12) J.-A. Chen, C.-S. Lin, and L. K. Liu, *J. Chin. Chem. Soc. (Taiwan)*, **43**, 95 (1996).

13) a) J. Gałecki, "Preparatyka nieorganiczna," WNT, Warsaw (1964), p. 439; b) Yu. V. Karyakin and I. I. Angelov, "Chistye khimicheskie reaktivy," Goskhimizdat, Moscow (1955), p. 333. Recently, it has been reported that the so-called Chemical Manganese Dioxide (CMD; Wako Pure Chemical Industries, Ltd., Japan), produced for dry battery manufacture, is particularly suitable for various selective oxidations, see: T. Aoyama, N. Sonoda, M. Yamaguchi, K. Toriyama, M. Anzai, A. Ando, and T. Shioiri, *Synlett*, **1998**, 35; M. Hirano, S. Yakabe, H. Chicamori, J. H. Clark, and T. Morimoto, *J. Chem. Res., Synop.*, **1998**, 308 and 310. It would be interesting to use this brand of MnO_2 in the oxidative iodination reactions reported in this paper.

14) We observed that this preparatory stirring period (2 h, room temperature) was indispensable to attain the high yields given in the Table 1. Presumably, transient *iodine(I)* and, particularly, *iodine(III)* species are formed all not at once, but they need some definite time to get possibly highest concentration levels.

15) P. Kaźmierczak and L. Skulski, *Bull. Chem. Soc. Jpn.*, **70**, 219 (1997).

16) P. Kaźmierczak and L. Skulski, *Synthesis*, **1998**, in printing. On pouring the reaction mixtures containing the assumed organic *iodine(III)* intermediates, $Ar-ISO_4$ or $Ar-I(OSO_3H)_2$, into excess aqueous ammonium acetate solutions, the corresponding (diacetoxyiodo)arenes, $Ar-I(OCOCH_3)_2$, were obtained in 58—82% yields.

17) *Varied quantities* of concd H_2SO_4 added to the reaction mixtures (established experimentally) clearly depended on relative reactivities of the iodinated arenes. More deactivated was arene, more

concd H_2SO_4 had to be added to increase the concentration of transient *iodine(I)* or *iodine(III)* species formed in the reaction mixtures.

18) "Dictionary of Organic Compounds," 6th ed, Chapman & Hall, London– Glasgow– Weinheim– New York– Tokyo– Melbourne– Madras (1996).

19) R. D. Desai and R. H. Kundel, *J. Indian Chem. Soc.*, **39**, 238 (1952).