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The Direct Iodination of Arenes with Chromium(VI) Oxide as the Oxidant

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An easy and cheap laboratory method is presented for the direct mono- and diiodination of a number of activated and deactivated arenes. The main iodination reactions occurred at the temperatures not exceeding 65 °C for 0.5—12 h in the *anhydrous*, strongly acidic liquid system, $I_2/AcOH/Ac_2O/H_2SO_4$, in the presence of prior dissolved CrO_3 used as the oxidant. The yields of the pure iodinated products varied from 31% (for 3,5-diiodobenzoic acid) up to 90% (for 4-iodoanisole). So far, benzonitrile and some oxidizable aromatics, e.g. naphthalene, fluorene, xanthene, and thiophene, have been found to be unsuitable for the effective iodination. Nevertheless, this novel, simple method of direct iodination is worthy to be extended to other appropriate aromatics.

Aromatic iodides are widely used in organic synthesis; hence many different methods, and their improvements, have been reported for their effective preparation.[1] In our former paper[2] we reported a simple and efficient laboratory method for monoiodination of *highly activated* arenes and heterocycles with molecular iodine in the presence of either pure lead(IV) acetate dissolved in glacial acetic acid, or with the same oxidant prepared in situ from minium, Pb_3O_4, in hot mixtures of acetic acid with acetic anhydride. Probably only transient *iodine(I)* species are acting there as the iodinating agents. We are still looking for new (or improved), cheap and easy procedures for the aromatic iodination. Hence, we have carried out the direct iodination of a number of arenes (Table 1) in an *anhydrous*, strongly acidic liquid medium, $I_2/CH_3COOH/(CH_3CO)_2O/H_2SO_4$, in the presence of prior dissolved chromium(VI) oxide, CrO_3, used as the oxidant. This versatile and cheap oxidant, used in the literature under various experimental conditions,[3] has been widely applied in organic synthesis,[4] except for the aromatic iodination reactions. Japanese chemists[5] iodinated *benzene* with iodine, in pressurized air or oxygen gas, in acidic solvents using twenty four metal salts as catalysts; they mentioned also *a chromate*. The iodination rate was dependent on the acidity of the solvent applied: $CF_3SO_3H > CH_3SO_3H > CF_3COOH >> CH_3COOH$. 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 sorts of counter ions of metal ions do not seem to be important. Later, Soviet authors[6] applied *chromium(VI) salts* for the aromatic iodination. They effectively iodinated only benzene and toluene (but failed to iodinate benzoic acid and nitrobenzene) with iodine in a mixture of CCl_4 with acetic acid containing H_2SO_4, using four dichromates as the oxidants. This method gave iodobenzene (61—88%) and a mixture of *p*- and *o*-iodotoluenes (69—75%; 3 : 1 ratio), respectively. They qualitatively arranged the oxidizing activity of the dichromates as follows: $K_2Cr_2O_7 < Na_2Cr_2O_7 < Li_2Cr_2O_7 < (NH_4)_2Cr_2O_7$. We assume that their failure to iodinate benzoic acid was mainly due to the presence of *water* in the reaction mixtures: They used water acidified with H_2SO_4 for prior dissolution of the dichromates. It is known[3,4,7] that water, due to its high hydration power, diminishes the oxidizing activity of inorganic oxidants. In contrast, this activity is increased when the overall acidity of the oxidizing mixtures is growing to some optimum extent. When this extent is considerably exceeded, then the iodination yields may drop strikingly, due to a predominant protonation of the reacted aromatic molecules.

Results and Discussion

The *anhydrous* conditions were attained in this work by dissolving CrO_3 in a cooled mixture of glacial acetic acid with acetic anhydride.[3] Subsequently, powdered diiodine was dissolved, followed (after one hour) by an appropriate arene. A concentrated (98%) H_2SO_4 was added dropwise with stirring while keeping the temperature below 30 °C (vide infra). Then, the main iodination reactions were accomplished at the temperatures not exceeding 65 °C, until the reaction mixtures changed their color to deep-green. It usually took 0.5—6.0 h; for benzoic acid; in Procedure 1, this time was exceptionally prolonged to 12 h. Finally, the resulting mixtures were worked up with particular workups (i)—(iii) given in the Experimental section. Assumingly, the said monoiodination reactions are occurring stepwise as follows:

Table 1. Iodinated Pure Products Prepared (Checked with TLC and ^1H NMR Spectra)

Substrate	Procedure[a]	Time/h[b] (Temp/°C)	Product (Its arabic denotation)		Yield %	Analysis/% I Calcd (Found)	Mp/°C/**solvent**[c] (Lit)[12]
C_6H_6	1 b,i (ii)	1.0; 2.0[d] (55—65)	PhI	**(1)**	68; 77[e]	62.20 (62.21)	bp 87—88/30 (bp 63—64/8; 188)
C_6H_6	2 b,iii	1.5 (55—65)	1,4-$I_2C_6H_4$	**(2)**	60	76.93 (76.51)	126—128/**E** (129)
PhI	1 b,iii	1.0 (55—65)	1,4-$I_2C_6H_4$	**(2)**	60	76.93 (76.46)	126—128/**E** (129)
PhBr	1 b,i (iii)	1.0 (55—65)	1-Br-4-IC_6H_4	**(3)**	68	44.86 (44.71)	91—92/**H** (91—92)
PhCl	1 b,i (iii)	1.0 (55—65)	1-Cl-4-IC_6H_4	**(4)**	67	53.22 (52.86)	56—57/**E** (57)
PhF	1 b,i (ii)	1.0 (55—65)	1-F-4-IC_6H_4	**(5)**	86	57.16 (57.26)	bp 182—183/760 (bp 182—184/760)
1,3-$Me_2C_6H_4$	2 b,iii	1.5 (55—65)	1,5-I_2-2,4-$Me_2C_6H_2$	**(6)**	81	70.90 (70.63)	71—72/**H** (72—74)
1,3,5-$Me_3C_6H_3$	1 b,ii	1.5 (55—65)	1,3,5-$Me_3C_6H_2I$	**(7)**	49	51.59 (51.46)	bp 141—142/50; 28—29/**P** (29—30)
4-$O_2NC_6H_4OMe$	1 b,iii	1.5 (55—65)	2-I-4-$O_2NC_6H_3OMe$	**(8)**	86	45.48 (45.07)	97—98/**H** (97)
4-$MeOC_6H_4COOH$	1 b,iii	1.5 (55—65)	3-I-4-$MeOC_6H_3COOH$	**(9)**	73	45.65 (45.52)	233—234/**E** (234.5 subl.)
4-$MeOC_6H_4COPh$	1 b,iii	1.5 (55—65)	3-I-4-$MeOC_6H_3COPh$	**(10)**	67	37.53 (37.21)	81—82/**H** (80; 81)[13]
PhNHCOMe	1 b,iii	1.5 (55—65)	4-$IC_6H_4NHCOMe$	**(11)**	69	48.62 (48.47)	188—189/**EA** (184)
PhOMe	1 a,i (iii)	0.5 (55—65)	4-IC_6H_4OMe	**(12)**	90	54.23 (54.08)	51—52/**H** (51—52)
PhOMe	2 a,iii	0.5 (55—65)	2,4-$I_2C_6H_3OMe$	**(13)**	58	70.52 (70.29)	68—69/**H** (68)
PhOEt	1 a,i (iii)	0.5 (55—65)	4-IC_6H_4OEt	**(14)**	68	51.17 (51.04)	bp 141—142/30; 27—29**P** (28—29)
1,2-$(MeO)_2C_6H_4$	2 a,iii	1.0 (55—65)	1,2-I_2-4,5-$(MeO)_2C_6H_2$	**(15)**	78	65.09 (65.32)	130—131/**H** (130—132)
PhCOOH	1 c,iii	12.0 (55—65)	3-IC_6H_4COOH	**(16)**	30[f]	51.17 (50.62)	184—186/**D** (187—188)
PhCOOH	3 a,iii	3.5, 1.0[g] (R.T., 45)	3-IC_6H_4COOH	**(16)**	86	51.17 (50.83)	184—186/**D** (187—188)
PhCOOH	4 c,iii	6.0, 1.0[h] (R.T., 60)	3,5-$I_2C_6H_3COOH$	**(17)**	31	67.89 (67.60)	232—233/**I** (235—236)
PhCOOMe	3 a,iii	3.0, 1.0[g] (R.T., 45)	3-IC_6H_4COOMe	**(18)**	66	48.44 (48.23)	52—53/**P** (54—55)
PhCOOEt	3 a,ii	3.0, 1.0[g] (R.T., 45)	3-IC_6H_4COOEt	**(19)**	64	45.98 (45.60)	bp 148—150/12 (bp 150.5/15)
PhCOPh	4 a,iii	3.0, 1.0[g] (R.T., 45)	3-$IC_6H_4COC_6H_4I$-3′	**(20)**	57	58.48 (58.35)	147—149/**A** (152.5—153.5)
PhCOCOPh	4 a,iii	3.0, 1.0[g] (R.T., 45)	3-$IC_6H_4COCOC_6H_4I$-3′	**(21)**	72	54.93 (54.40)	130—131/**E** (128—129)[14]
$PhCONH_2$	3 b,iii	4.0, 1.0[g] (R.T., 45)	3-$IC_6H_4CONH_2$	**(22)**	88	51.38 (51.12)	186—187/**E** (186.5)
$PhSO_2NH_2$	3 c,iii	5.0, 1.0[g] (R.T., 45)	3-$IC_6H_4SO_2NH_2$	**(23)**	74	44.83 (44.50)	152—153/**E** (153)[15]
$PhSO_2Ph$	4 c,iii	3.0, 1.0[h] (R.T., 60)	3-$IC_6H_4SO_2C_6H_4I$-3′	**(24)**	83	53.99 (53.60)	123—124/**N** (122—123)[16]
$PhNO_2$	3 c,ii	6.0, 1.0[g] (R.T., 45)	3-$IC_6H_4NO_2$	**(25)**	71	50.96 (50.69)	bp 158—160/22; 33—34/**P** (bp 153/14; 38)

a) See Experimental for the denotations used below. b) Time and temperature of the *main iodination reaction* run after adding and dissolving all the reactants. c) Solvents used for crystallization: **A**, Me_2CO; **B**, benzene; **C**, CCl_4; **D**, CH_3Cl; **E**, EtOH; **EA**, twice from EtOH–25% aq ammonia (5 : 1 v/v) and once from benzene; **H**, hexane (or EtOH); **I**, isopropyl alcohol; **N**, 1-butanol; **P**, petroleum ether. d) A change in the sequence of adding the substrates from $AcOH+Ac_2O/CrO_3/I_2/Ar\text{-}H/H_2SO_4$ to $AcOH+Ac_2O/Ar\text{-}H/I_2/CrO_3/H_2SO_4$ resulted in a lengthening the iodination time from 1.0 to 2.0 h, respectively. e) By enlarging fivefold the preparative scale given in Experimental, we obtained iodobenzene (**1**) in 77% yield. f) This result is given here only for the sake of comparison. g) After keeping the reaction mixtures for 3.0—6.0 h at *room temperature*, the iodination reactions were completed by the following one-hour heating at 45 °C. h) After keeping the reaction mixture for either 3.0 h (**24**) or 6.0 h (**17**) at *room temperature*, the iodination reaction was completed by the following one-hour heating at 60 °C.

$$2\text{Ar-H} + 2\text{CrO}_3 + \text{I}_2 + 6\text{Ac}_2\text{O} + 7\text{H}_2\text{SO}_4 \longrightarrow \mathbf{2Ar\text{-}I(OSO_3H)_2} + \text{Cr}_2(\text{SO}_4)_3 + 12\text{AcOH}^{\text{a)}} \quad (1)$$

$$2\text{Ar-I(OSO}_3\text{H)}_2 + 2\text{I}_2 + 4\text{Ar-H} \longrightarrow 6\text{Ar-I} + 4\text{H}_2\text{SO}_4 \quad (2)$$

$$6\text{Ar-H} + 2\text{CrO}_3 + 3\text{I}_2 + 6\text{Ac}_2\text{O} + 3\text{H}_2\text{SO}_4 \xrightarrow{\text{AcOH}} 6\mathbf{Ar\text{-}I} + \text{Cr}_2(\text{SO}_4)_3 + 12\text{AcOH}^{\text{b)}} \quad (3)$$

a) The stoichiometry obeyed in Procedure 3, suitable for highly deactivated arenes (see Experimental).

b) The stoichiometry obeyed in Procedure 1, suitable for activated arenes, benzene, and halobenzenes (see Experimental).

Kaźmierczak and Skulski[8] have recently established in our laboratory that, by applying the reaction stoichiometry according to Eq. 1, it is possible to isolate in good yields several *(diacetoxyiodo)arenes* by pouring the final reaction mixtures into excess aqueous ammonium acetate solutions; this will be published soon. It proves that some transient *iodine(III)* species are present in the reaction mixtures obeying Eq. 1 and acting there as stronger electrophiles. Next, the assumed intermediate organic *iodine(III)* derivatives, Ar-I$(\text{OSO}_3\text{H})_2$, would react with excess molecular iodine to form some less reactive, transient *iodine(I)* species acting upon excess Ar–H, in agreement with Eq. 2. Altogether, in Procedure 1, this would yield no more than six moles of the final products, Ar-I; see Ref. 9 explaining the formation of the transient *iodine(I)* species. We have also observed that concentrated (98%) H_2SO_4 should be slowly added dropwise to the reaction mixtures below 30 °C. Otherwise, e.g. at 50 °C or higher, some undesirable, oxidative side-reactions due to H_2SO_4 are observed, resulting in the evolution of sulfur dioxide. The control over the iodination reactions is difficult then, and the yields of the iodinated products are considerably lowered. In Procedure 2 (Experimental) we deliberately altered the sequence of adding the reactants and their relative amounts in order to obtain the highest possible yields of the *diiodinated* products.

By applying Procedures 1 and 2 for the aromatic iodination of benzene and some activated arenes listed in the Table 1, we succeeded to obtain the corresponding either mono- or diiodinated products in 49—90% yields. In spite of many attempts, working under widely varied reaction conditions, we practically failed to iodinate nitrobenzene. For a less strongly deactivated arene, benzoic acid, the final yield was low, i.e. 30%. However, halobenzenes were iodinated in 60—86% yields (Table 1).

Some oxidizable aromatics cannot be effectively iodinated with the presented method: e.g. naphthalene, fluorene, xanthene, and thiophene. For example, on the monoiodination of fluorene we found in the final reaction mixture both 2-iodo- and 2,7-diiodofluorenes, strongly contaminated with fluoren-9-one and with its iodinated derivatives (TLC). Mixtures of the iodo derivatives were obtained by the iodination of some arenes, which was evidenced by the ^{1}H NMR spectra and TLC. The effective monoiodination of toluene (88%) resulted in a mixture of *o*- and *p*-iodotoluenes (1 : 2 ratio). 2,4-Diiodotoluene (79%) was, in fact, mixed with 2,6-diiodotoluene (5 : 1 ratio). 1,2- and 1,3-Xylenes gave the mixtures of iodoxylenes with small admixtures of diiodoxylenes in 89 and 74% yields, respectively. It is difficult to separate such mixtures with common laboratory methods, e.g. distillation or repeated recrystallizations. More advanced methods are necessary, e.g. the preparative chromatography.

From the above it is seen that Procedures 1 and 2 are inappropriate for the iodination of highly deactivated arenes, giving, at the best, only low yields of the pure iodinated products. Hence, we changed the overall stoichiometry of the iodination reactions for some deactivated arenes (benzoic acid, methyl and ethyl benzoates, benzamide, benzenesulfonamide, and nitrobenzene) in approximate agreement with Eq. 1 (Procedure 3). Since more electrophilic, transient *iodine(III)* species are mainly acting there in the aromatic substitution, after pouring the final reaction mixtures into excess aqueous Na_2SO_3 solution[10] buffered with $(\text{NH}_4)_2\text{CO}_3$ to neutralize H_2SO_4, the iodination yields were considerably increased, as expected. In this way we obtained pure 3-iodobenzoic acid (86%), methyl 3-iodobenzoate (66%), ethyl 3-iodobenzoate (64%), 3-iodobenzamide (88%), 3-iodobenzenesulfonamide (74%), and 3-iodonitrobenzene (71%). When benzonitrile was repeatedly monoiodinated with Procedure 3, the expected 3-iodobenzonitrile (ca. 10%) was strongly contaminated with 3-iodobenzamide (ca. 30%), benzamide, benzonitrile, etc. (TLC). Hence, we did not study this reaction further. Our attempts to obtain solely the *monoiodinated* products from benzophenone, dibenzoyl (benzil), and diphenyl sulfone were unsuccessful: on varying the sequence of adding the reactants in Procedure 3, as well as on adding excess quantities (up to 50%) of the starting arenes, we always obtained three-component mixtures of the mono- and diiodinated products along with the unreacted starting arenes (TLC, ^{1}H NMR). In Procedure 4 we altered the relative amounts of the reactants, which resulted in good yields of the pure *diiodinated* products, viz. 3,3′-diiodobenzophenone (57%), 3,3′-diiododibenzoyl (72%), and 3,3′-diiododiphenyl sulfone (83%); we also succeeded to obtain 3,5-diiodobenzoic acid (31%). For more details see the Experimental section and the Table 1.

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) and ^{1}H NMR spectra compared either with those of the authentic specimens or with those submitted in the literature. Sometimes, the ^{1}H NMR spectra of the corresponding chloro or bromo derivatives were used for the comparison. The structures were also corroborated by elemental analyses.

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 and CrO_3 should be *finely powdered* in order to facilitate their dissolution. ^{1}H NMR spectra (not submitted here) were taken with a Tesla BS 567 A (100 MHz) spectrometer in the same solvents as those used in the literature for the sake of a better comparison. Elemental analyses were carried out at the Institute of Organic Chemistry, the Polish Academy of Sciences, Warsaw.

The toxic residues containing chromium salts left after the iodination reactions were collected and disposed of according to the local safety measures. Working in the laboratory scale, we did not recover cheap chromium salts from the residues.

Procedure 1: The Monoiodination of Some Activated Arenes: (see the *Table 1* for more details and the Arabic denotations used below for the iodinated compounds)

Powdered CrO_3 (3.63 g; 36.3 mmol; 10% excess established to be the most appropriate) was slowly added portionwise, with stirring and external cooling, to a mixture of glacial AcOH (10 ml) with Ac_2O (30 ml; 318 mmol), keeping the temperature ***below 40 °C*** (the reaction is strongly exothermic).[4] After the dissolution of CrO_3, powdered I_2 (12.7 g; 50 mmol; 0% excess) was added portionwise with stirring while keeping the temperature below 45—50 °C (exothermic reaction). After the materials dissolved, the mixture was stirred for 1 h with no heating. A chosen arene (110 mmol; 10% excess with respect to I_2 consumed) was added, and after its dissolution, a concentrated (98%) H_2SO_4 was *slowly* added dropwise with efficient stirring and external cooling, keeping the temperature ***below 30 °C*** (the reaction is strongly exothermic); *its quantities* depended on the reactivity of the iodinated substrates, viz.

(a) for highly activated arenes (anisole and phenetole), 2.45 g (1.33 ml; 25 mmol) of concentrated (98%) H_2SO_4 was added dropwise below 30 °C;

(b) for most of the arenes listed in the Table 1, 4.90 g (2.66 ml; 50 mmol) of concentrated (98%) H_2SO_4 was added dropwise below 30 °C;

(c) for deactivated arenes, e.g. benzoic acid, 14.71 g (8.00 ml; 150 mmol) of concentrated (98%) H_2SO_4 was added dropwise below 30 °C.

Subsequently, the *main iodination reactions* were carried out for 0.5—12 h (Table 1) at temperatures not exceeding 65 °C, until the coloration of the reaction mixtures became deep-green. These *final reaction mixtures* were worked up as follows:

(i) the *steam-volatile* products, e.g. iodobenzene (**1**) and some of its derivatives **3**—**5**, **12**, and **14**, may be purified by steam distillation (superheated steam may be applied for higher boiling compounds to shorten the distillation times). Before the distillation, an excess of aq Na_2SO_3 was added to the final reaction mixtures to destroy any unreacted iodine. The distillates were extracted with $CHCl_3$, and the collected extracts were elaborated as those in workup (ii) below. Alternatively, the separated *solid* products were collected by filtration, washed with water, dried, and further worked up as those in workup (iii) below. All the chromium salts were left in the remainders after the distillations;

(ii) the final reaction mixtures were poured into crushed ice (200 g). The *oily* crude products were extracted with $CHCl_3$ (3×30 ml); the collected extracts were washed with 3% aq $NaHSO_3$ and water, dried over $MgSO_4$, the solvent was distilled off, and the residues were fractionated under vacuum (Table 1) to give the purified products **1**, **5**, and **7**. The chromium salts were left in the aqueous layers;

(iii) the final reaction mixtures were poured into crushed ice (200 g). The precipitated *solid* crude products were collected by filtration, washed well with cold water, 3% aq $NaHSO_3$, and again with cold water, until the washings became colorless. The products were dried in the air and then in a vacuum desiccator over P_2O_5 or KOH. They were recrystallized, sometimes with activated carbon, from appropriate solvents (Table 1) to give the purified products **2**—**4**, **8**—**12**, **14**, and **16**. All the chromium salts were washed off into the filtrates.

The yields for the *monoiodinated* products given in the Table 1 are calculated from the total amounts of the *iodine* used in the reactions.

Procedure 2: The Diiodination of Some Activated Arenes: Powdered I_2 (13.97 g; 55 mmol; 10% excess with respect to the diiodinated arene) was suspended in a mixture of glacial AcOH (10 ml) with Ac_2O (30 ml; 318 mmol). Powdered CrO_3 (3.63 g; 36.3 mmol; 10% excess) was slowly added portionwise, with vigorous stirring and external cooling ***below 40 °C*** (the reaction is strongly exothermic).[4] After the dissolution of CrO_3 and the iodine (exothermic reactions), the mixture was stirred for 1 h with no heating. Next, a chosen arene (50 mmol; 0% excess) was added. After its dissolution, some concentrated (98%) H_2SO_4 [either (a) 2.45 g; 1.33 ml; 25 mmol or (b) 4.90 g; 2.66 ml; 50 mmol] was *slowly* added dropwise with stirring, always keeping the temperature ***below 30 °C*** (the reaction is strongly exothermic). Finally, the *main iodination reactions* were carried out at temperatures not exceeding 65 °C for 0.5 —1.5 h (Table 1), until the *final reaction mixtures* became deep-green. The following workup (iii) was the same as that in Procedure 1. In this way we obtained the purified diiodinated arenes **2**, **6**, **13**, and **15** (Table 1).

The yields for the *diiodinated* products given in the Table 1 are calculated from the total amounts of the *arenes* used in the reactions.

Procedure 3: The Monoiodination of Some Deactivated Arenes: A cold solution of CrO_3 (6.25 g; 62.5 mmol; 25% excess established to be the most appropriate) in a mixture of glacial AcOH (40 ml) with Ac_2O (20 ml; 212 mmol) was prepared as that in Procedure 1. Powdered I_2 (7.94 g; 31.2 mmol; 25% excess with respect to the iodinated arenes) was slowly added portionwise with stirring ***below 40 °C***, followed (after 1 h) by concentrated (98%) H_2SO_4 which was slowly added dropwise ***below 30 °C***, with efficient stirring and external cooling; *its quantities* depended on the reactivity of the iodinated substrates; viz.

(a) for benzoic acid, methyl benzoate, and ethyl benzoate, 34.33 g (18.66 ml; 350 mmol) of concentrated (98%) H_2SO_4 was added dropwise below 30 °C;

(b) for benzamide, 51.00 g (27.71 ml; 520 mmol) of concentrated (98%) H_2SO_4 was added dropwise below 30 °C;

(c) for benzenesulfonamide and nitrobenzene, 68.66 g (37.31 ml; 700 mmol) of concentrated (98%) H_2SO_4 was added dropwise below 30 °C. Next, a chosen deactivated arene (50 mmol; 0% excess) was added with stirring. After the dissolution of the reactants, the whole was stirred for 3.0—6.0 h (Table 1) at *room temperature*, followed by the one-hour heating period at 45 °C to complete the reaction. The resulting deep-green solution was poured, with stirring, into ice-water (150 g) containing prior dissolved Na_2SO_3 (12.6 g; 100 mmol)[10] and $(NH_4)_2CO_3$ (50 g; 520 mmol) (*foaming*). After 1 h, the precipitates were collected by filtration, washed well with cold water, until the washings were colorless, dried, and recrystallized from appropriate solvents (Table 1) to give the purified products **16**, **18**, **22**, and **23**. Ethyl benzoate and nitrobenzene gave the *oily* crude products, which were worked up with the workup (ii) in Procedure 1 to give the purified products **19** and **25** (Table 1).

Note. When this work was nearly completed, we observed that on leaving the final reaction mixtures, with no heating, for one week at *room temperature*, the yields of the iodinated products given in the Table 1 were increased by ca. 5—10%.

When *benzene* was iodinated with Procedure 3, the yield of iodobenzene (**1**) was lowered to 10%. 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 dried. After *quick* recrystallization from MeOH, we obtained pure **diphenyliodonium iodide** (44%), mp 230—232 °C (decomp), lit,[11] mp 234—235 °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. 11. This novel "*one-pot*" method of preparing the symmetric diaryliodonium salts is presently being improved and extended,[8] and will be published soon.

Procedure 4: The Diiodination of Some Deactivated Arenes: A cold solution made of CrO_3 (6.25 g; 62.5 mmol; 25% excess), glacial AcOH (40 ml), Ac_2O (20 ml; 212 mmol), I_2 (7.94 g; 31.2 mmol; 25% excess with respect to the diiodinated arenes), and concentrated (98%) H_2SO_4 [either (a) 34.33 g; 18.66 ml; 350 mmol or (c) 68.66 g; 37.31 ml; 700 mmol] was strictly prepared like that in Procedure 3. A chosen deactivated arene (25 mmol; 0% excess) was added. After the dissolution of the reactants, the whole was stirred for 3.0—6.0 h (Table 1) at *room temperature*, followed by the one-hour heating period either at 45 °C or at 60 °C to complete the reaction (Table 1). The whole was poured into ice-water (150 g) containing prior dissolved Na_2SO_3 (12.6 g; 100 mmol)[10] and $(NH_4)_2CO_3$ (50 g; 520 mmol) (*foaming*). The following workup (iii) for the *solid* crude products was the same as that in Procedure 1 to give the purified products **17**, **20**, **21**, and **24** (Table 1).

In Procedures 3 and 4, the yields of the *mono-* or *diiodinated* products given in the Table 1 are calculated from the total amounts of the *arenes* used in the reactions.

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$$\text{Ar-I(OSO}_3\text{H)}_2 + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \textbf{Ar-I} + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4.$$

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