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Oxidative Anion Metatheses in Diaryliodonium Iodides and Chlorides

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Oxidative anion metatheses in the *crude* title iodides and chlorides produced the corresponding *pure* hydrogensulfates, nitrates, tetrafluoroborates, triflates, tosylates, as well as bromides and chlorides (only from the iodides) in 54—86% yields. These procedures are easier and shorter than earlier methods. By using modified oxidative metatheses in the title iodides (in the presence of HBr or HCl) it was possible either to isolate, or to detect only, the intermediate dihaloiodates(I), $[Ar_2I]^+[IX_2]^-$ ($X = Br$ or Cl). A complex $Ph_2I^+Cl^-\cdot 1/2I_2$ was also obtained in 56% yield. Tetraethylammonium iodide was similarly converted into pure tetrafluoroborate or dibromoiodate(I) in 75 and 76% yields, respectively.

Symmetric and unsymmetric diaryliodonium salts, $[Ar_2I]^+X^-$ and $[Ar–I–Ar']^+X^-$, with a large variety of inorganic and organic counter ions, X^-, are useful for photopolymerization processes and chemical amplification in imaging systems; some of them display a biological (e.g. antimicrobial) activity.[1—3] They are also applied for the arylation of nucleophilic reagents,[2—6] particularly those with substantially *non-nucleophilic* counter ions, such as tetrafluoroborate, tosylate, hexafluoroantimonate. The direct syntheses of trifluoromethanesulfonates (triflates) have recently been published by Japanese workers.[7] In many cases, *crude* diaryliodonium salts are precipitated *in high yields* from the final reaction mixtures in the form of sparingly soluble iodides or bromides[2,3,6] (seldom, perchlorates),[8] which are hard to get into solution for further reactions or purification. These may, however, be metathesized into the respective salts with *non-nucleophilic* (and many others) counter ions using a variety of preparative approaches,[3—5] which have also been briefly reviewed.[2]

It has been known to us[9] that *ionic* inorganic and organic halides in hot (or boiling) solutions/suspensions, acidified with e.g. H_2SO_4 or other strong inorganic/organic acids, are more or less readily oxidized ($I^- > Br^- \gg Cl^-$; fluorides do *not* react) by an excess of 30% H_2O_2, with the evolution of the respective molecular halogens, which can be used, so far, solely for halogenation. In former work[8] we applied this information to metathesize *oxidatively* a number of *crude* diaryliodonium bromides into the respective *pure* tetrafluoroborates, tosylates, trifluoroacetates, hydrogensulfates, nitrates, and chlorides in 57—80% yields; in this work we similarly metathesized diphenyliodonium bromide (**1c**) into triflate **1d** in 83% yield. Below, we report on a number of exemplary *oxidative* anion metatheses in six *crude* diaryliodonium iodides **1—6, a** (Table 1) and two chlorides **1b**, **7b** into the respective *pure* hydrogensulfates, nitrates, tetrafluoroborates, triflates, tosylates, as well as into bromides

Table 1. Preparative Details, Yields and Mp of Diaryliodonium Iodides **1—6, a**[a)]

ArI	ArH	Reaction's temp/°C	Reaction's time/min	Product	Crude yield/%	Mp/°C with decomp[b)] (lit)	Analysis/% Calcd (Found) C	H	I	N
PhI	C_6H_6	50	90	**1a**	55	166—167 (159—162,	35.32	2.47	62.20	—
						172—175, 175—176, 182[18)])	(35.20	2.52	62.24	—)
PhI	1,4-$Me_2C_6H_4$	R.T.	15	**2a**	64	160—161 (161[18)])	38.56	3.24	58.20	—
							(38.50	3.13	58.18	—)
PhI	PhNHCOMe	R.T.	15	**3a**	50	177—179 (174, 178—179[18)])	36.16	2.82	54.57	3.01
							(36.08	2.66	54.69	3.14)
2-$IC_6H_4NO_2$	PhOMe	R.T.	15	**4a**	86	125—126	32.32	2.30	52.54	2.90
							(32.14	2.16	52.42	2.85)
2-ClC_6H_4I	PhOMe	R.T.	15	**5a**	80	140—141	33.05	2.35	53.72	—
							(33.03	2.26	53.63	—)
2-ClC_6H_4I	1,3-$Me_2C_6H_4$	R.T.	15	**6a**	89	145—146	35.74	2.78	53.94	—
							(35.77	2.72	53.78	—)

a) These compounds were obtained solely with the short-cut method previously reported in Ref. 8. For the denotations **1—6, a** see Scheme 1.

b) Mp are given for the purified products **1—6, a**. They should be recrystallized from MeOH *as quickly as possible*.[8)]

Table 2. Preparative Details, Yields and Mp of Purified Diaryliodonium Salts Obtained by the Oxidative Anion Metatheses

Substrate	HX	Reaction's solvent	Product	Yield/%	Mp/°C (lit)	Molecular formula	Analysis/% Calcd (Found)			
							C	H	I	N
1a	HCl	MeOH	**1b**	73	231 decomp$^{a)}$ (MeOH/Et_2O)	$C_{12}H_{10}ClI$	45.33	3.18	40.09	—
					(229—230$^{8)}$)		(45.18	3.09	40.12	—)
1a	HBr	MeOH	**1c**	92$^{b)}$	234—235 decomp$^{a)}$ (MeOH)	$C_{12}H_{10}BrI$	39.92	2.79	35.15	—
					(234—235$^{8)}$)		(39.80	2.68	35.22	—)
1a	TfOH	EtOH	**1d**	77	178—180 (*n*-PrOH/Et_2O)	$C_{13}H_{10}F_3ISO_3$	36.30	2.34	29.50	—
					(179—184,$^{7)}$ 178—180$^{19)}$)		(36.30	2.35	29.67	—)
1a	H_2SO_4	EtOH	**1e**	77	167—169 decomp (EtOH/Et_2O)	$C_{12}H_{11}ISO_4$	38.11	2.93	33.56	—
					(167—168,$^{20)}$ 167—170$^{8)}$)		(38.06	3.08	33.59	—)
1a	HBF_4	*n*-PrOH	**1f**	76	135—137 (CH_2Cl_2/CCl_4)	$C_{12}H_{10}BF_4I$	39.17	2.74	34.49	—
					(135—137$^{8)}$)		(39.13	2.74	34.62	—)
1a	HNO_3	96%EtOH	**1g**	78	152—154 decomp (EtOH/Et_2O)	$C_{12}H_{10}INO_3$	42.01	2.94	36.99	4.08
					(147—150,$^{8)}$153—154$^{18)}$)		(41.87	2.79	36.89	4.15)
1a	TsOH	EtOH	**1h**	78	186—187 decomp (EtOH/Et_2O)	$C_{19}H_{17}ISO_3$	50.45	3.79	28.06	—
					(190—192$^{8)}$)		(50.51	3.76	28.20	—)
1a	HBr	MeOH	**1i**	56	145—146 decomp (MeOH)	$C_{12}H_{10}I_2Br_2$	25.38	1.78	44.70	—
					(140,143$^{18)}$)		(25.35	1.80	44.52	—)
1b	H_2SO_4	MeOH	**1e**	69	167—170 decomp (EtOH/Et_2O)	$C_{12}H_{11}ISO_4$	—	—	33.56	—
					(see above)		(—	—	33.48	—)
1b	HBF_4	MeOH	**1f**	76	135—137 (CH_2Cl_2/CCl_4)	$C_{12}H_{10}BF_4I$	—	—	34.49	—
					(see above)		(—	—	34.52	—)
1b	TsOH	MeOH	**1h**	62	186—188 decomp (EtOH/Et_2O)	$C_{19}H_{17}ISO_3$	—	—	28.06	—
					(see above)		(—	—	27.95	—)
1c	TfOH	MeOH	**1d**	83	178—180 (*n*-PrOH/Et_2O)	$C_{13}H_{10}F_3ISO_3$	—	—	29.50	—
					(see above)		(—	—	29.62	—)
2a	TfOH	EtOH	**2d**	67	136—137 (($CH_2Cl)_2$/CCl_4)	$C_{15}H_{14}F_3ISO_3$	39.32	3.08	27.69	—
					(136—139$^{7)}$)		(39.24	3.04	27.72	—)
2a	H_2SO_4	EtOH	**2e**	78	150—153 decomp (EtOH/Et_2O)	$C_{14}H_{15}ISO_4$	41.39	3.72	31.24	—
							(41.46	3.68	31.36	—)
2a	HBF_4	*n*-PrOH	**2f**	74	196—198 decomp (*n*-PrOH/Et_2O)	$C_{14}H_{14}IBF_4$	42.47	3.56	32.05	—
							(42.43	3.51	32.09	—)
2a	HNO_3	96%EtOH	**2g**	82	177—178 decomp (96%EtOH/Et_2O)	$C_{14}H_{14}INO_3$	45.30	3.80	34.19	—
							(45.32	3.74	33.96	—)
3a	TfOH	EtOH	**3d**	83	201—203 decomp (96%EtOH/Et_2O)	$C_{15}H_{13}F_3INSO_4$	36.98	2.69	26.05	2.87
							(37.09	2.56	25.99	2.90)
3a	HBF_4	EtOH	**3f**	82	96—100 decomp$^{c)}$ (EtOH/Et_2O)	$C_{14}H_{13}BF_4INO$	39.57	3.08	29.85	3.30
							(39.53	3.14	29.81	3.30)
3a	TsOH	EtOH	**3h**	86	208—210 decomp (MeOH/Et_2O)	$C_{21}H_{20}INO_4S$	49.52	3.96	24.91	2.75
							(49.40	3.83	25.00	2.73)
4a	H_2SO_4	EtOH	**4e**	80	165—166 decomp (EtOH/Et_2O)	$C_{13}H_{12}INO_7S$	34.45	2.67	28.00	3.09
							(34.42	2.72	27.88	3.09)
4a	HBF_4	*n*-PrOH	**4f**	70	173—174 (*n*-PrOH/Et_2O)	$C_{13}H_{11}BF_4INO_3$	35.25	2.50	28.65	3.16
							(35.18	2.32	28.48	3.15)
4a	HNO_3	96%EtOH	**4g**	72	163—164 decomp (96%EtOH/Et_2O)	$C_{13}H_{11}IN_2O_6$	37.34	2.65	30.35	6.70
							(37.26	2.62	30.35	6.70)
5a	TfOH	EtOH	**5d**	77	167—168 (*n*-PrOH/Et_2O)	$C_{14}H_{11}ClF_3ISO_4$	33.99	2.24	25.66	—
							(34.00	2.20	25.68	—)
5a	HBF_4	*n*-PrOH	**5f**	67	159—161 (($CH_2Cl)_2$/CCl_4)	$C_{13}H_{11}BClF_4IO$	36.11	2.56	29.35	—
							(36.01	2.52	29.46	—)
5a	HNO_3	96%EtOH	**5g**	75	149—151 decomp (EtOH/Et_2O)	$C_{13}H_{11}ClINO_4$	38.31	2.72	31.14	3.44
							(38.30	2.64	31.04	3.66)
5a	TsOH	EtOH	**5h**	77	156—159 decomp (EtOH/Et_2O)	$C_{20}H_{18}ClIO_4S$	46.48	3.51	24.56	—
							(46.50	3.46	24.64	—)
6a	HCl	EtOH	**6b**	90$^{b)}$	195 decomp (MeOH)	$C_{14}H_{13}Cl_2I$	44.36	3.46	33.48	—
							(44.22	3.42	33.51	—)
6a	HBr	EtOH	**6c**	86$^{b)}$	188—189 decomp (MeOH)	$C_{14}H_{13}ClBrI$	39.70	3.09	29.96	—
							(39.56	3.12	30.00	—)
6a	TfOH	EtOH	**6d**	63	130—132 (($CH_2Cl)_2$/CCl_4)	$C_{15}H_{13}ClF_3ISO_3$	36.57	2.66	25.76	—
							(36.57	2.64	25.82	—)

Table 2. (Continued)

Substrate	HX	Reaction's solvent	Product	Yield/%	Mp/°C (lit)	Molecular formula	Analysis/% Calcd (Found)			
							C	H	I	N
6a	H_2SO_4	EtOH	**6e**	68	161—164 decomp (EtOH/Et_2O)	$C_{14}H_{14}ClISO_4$	38.16	3.20	28.80	—
							(38.20	3.22	28.78	—)
6a	HNO_3	96%EtOH	**6g**	84	173—174 decomp (96%EtOH/Et_2O)	$C_{14}H_{13}ClINO_3$	41.46	3.23	31.29	3.45
							(41.54	3.10	31.06	3.55)
6a	TsOH	EtOH	**6h**	86	199—201 decomp (EtOH/Et_2O)	$C_{21}H_{20}ClISO_3$	49.00	3.92	24.65	—
							(49.14	3.86	24.74	—)
7b	H_2SO_4	MeOH	**7e**	54	158—161 decomp (EtOH/Et_2O)	$C_{13}H_{12}ClISO_5$	35.27	2.73	28.67	—
							(35.12	2.68	28.51	—)
7b	HBF_4	MeOH	**7f**	76	183—185 (*n*-PrOH/Et_2O)	$C_{13}H_{11}BClF_4IO$	36.11	2.56	29.35	—
					(186—188[8])		(35.96	2.48	29.08	—)
7b	TsOH	MeOH	**7h**	64	187—189 decomp (EtOH/Et_2O)	$C_{20}H_{18}ClISO_4$	46.48	3.51	24.56	—
							(46.46	3.55	24.32	—)

a) Decomposition with the evolution of gaseous products. b) Crude yield. An analytical sample was *quickly* recrystallized from MeOH; see Ref. 8 for the explanation. c) Decomposition with the formation of some new crystals melting at 175—177 °C; lit,[22] mp 184 and 152 °C were reported for *p*-iodoacetanilide and *p*-fluoroacetanilide, respectively.

$$\underset{\mathbf{1—7,\ a—c}}{2[\mathrm{Ar{-}I{-}Ar'}]^+\mathrm{Y}^-} + 2\mathrm{HX} + \mathrm{H_2O_2} \xrightarrow[54—86\%]{\mathrm{ROH(reflux)},\ 10—180\,\mathrm{min}} \underset{\mathbf{1—7,\ d—h}}{2[\mathrm{Ar{-}I{-}Ar'}]^+\mathrm{X}^-} + \mathrm{Y_2} + 2\mathrm{H_2O}$$

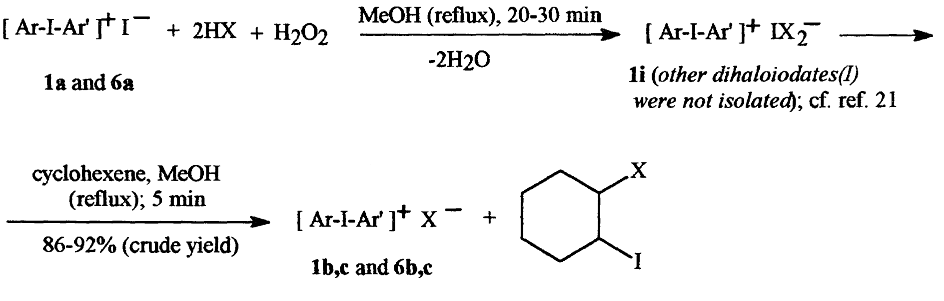
where: **1**—**7** diaryliodonium cations; **a**—**i** the accompanying counter ions.

	Ar	Ar′
1	Ph	Ph
2	Ph	2,5-$Me_2C_6H_3$
3	Ph	4-$MeCONHC_6H_4$
4	2-$O_2NC_6H_4$	4-$MeOC_6H_4$
5	2-ClC_6H_4	4-$MeOC_6H_4$
6	2-ClC_6H_4	2,4-$Me_2C_6H_3$
7	4-ClC_6H_4	4-$MeOC_6H_4$

	Y and X
a	I
b	Cl
c	Br
d	CF_3SO_3
e	HSO_4
f	BF_4
g	NO_3
h	TsO
i[a]	IBr_2

a) Dibromoiodate(I) **1i** was synthesized otherwise (Scheme 2).

Scheme 1.



where: HX = HBr or HCl; for other denotations see Scheme 1. Only1i was isolated in 56% yield as the *intermediate*. 1-X(Cl or Br)-2-iodocyclohexane was *washed off* in full from the crude products 1b,c and 6b,c with anhydrous diethyl ether.

Scheme 2.

and chlorides (only from the iodides) in 54—86% yields (Table 2); see Scheme 1.

Results and Discussion

Diaryliodonium chlorides were oxidized by H_2O_2 in acidified, boiling alcoholic solutions *much less readily* (3 h; 1076% excess of H_2O_2) than the respective bromides[8] (15 min; 196% excess of H_2O_2) and iodides (10 min; 36% excess of H_2O_2); the final yields of the pure metathesized products were 54—76, 57—80,[8] and 54—86%, respectively. As for the bromides,[8] and also for the chlorides the reactive molecular halogens, Br_2 and Cl_2, evolved in the oxidative reactions, were fully captured by the 100% excess of *cyclohexene* added on purpose as a "halogen scavenger". 1,2-Di-X-cyclohexanes (X=Br, Cl) as well as the other possible *cyclohexene adducts* with reactive agents (H_2O_2, $X\text{-}\overset{+}{O}H_2$, etc.) were subsequently removed from the crude products by their trituration with anhydrous diethyl ether, followed by washing on the filter with the same solvent; the following single recrystallization gave analytically pure metathesized products. For the iodides, the diiodine evolved was simply *washed off* from the crude metathesized products with anhydrous diethyl ether.[10]

In a former study[8] we metathesized oxidatively diphenyliodonium and 4-chlorophenyl-4′-methoxyphenyliodonium bromides into the respective chlorides in 63 and 68% yields, with no comments. However, in this work we found that such oxidative reactions are more complex than expected. This is likely to be due to a series of fast consecutive reactions taking place in the investigated solutions of diaryliodonium iodides containing H_2O_2, and acidified with a strong acid, (a)—(d):

$$\text{(a)}\quad I^-(\textit{apart})+H_2O_2\xrightarrow[-H_2O]{H^+}I\text{–}OH\xrightarrow{H^+}I\text{–}\overset{+}{O}H_2$$

$$\text{(b)}\quad I^-(\textit{unoxidized rest})+I\text{–}\overset{+}{O}H_2\xrightarrow[-H_2O]{}I_2(\textit{evolved};\text{see Scheme 1})^{11)}$$

$$\text{(c)}\quad Br^-(\textit{from excess HBr})+I\text{–}\overset{+}{O}H_2\xrightarrow[-H_2O]{}IBr(\textit{transient})$$

$$\xrightarrow{Br^-}IBr_2^-(\textit{intermediate})^{12)}$$

$$\text{(d)}\quad Cl^-(\textit{from excess HCl})+I\text{–}\overset{+}{O}H_2\xrightarrow[-H_2O]{}ICl(\textit{transient})$$

$$\xrightarrow{Cl^-}ICl_2^-(\textit{intermediate})^{12)}$$

The following Scheme 2 would explain our results obtained in the oxidative metatheses of diaryliodonium iodides into the corresponding chlorides and bromides; for more details see Experimental.

For the sake of a comparison, we also oxidatively metathesized tetraethylammonium iodide into the respective pure tetrafluoroborate (75%) and dibromoiodate(I) (76%). It was also possible to convert diphenyliodonium iodide (**1a**) into the complex $Ph_2I^+Cl^-\cdot 1/2I_2$ (56%); see Experimental.

Some "model" study was recently performed in our laboratory[13] on quite similar oxidative metatheses in boiling aqueous methanolic solutions of KI, KBr, and KCl. Each of the halides was effectively converted into pure potassium hydrogensulfate, tetrafluoroborate, and tosylate. This also confirms the usefulness of the presented oxidative method in *inorganic* chemistry.

Experimental

2-Chloroiodobenzene and 2-iodonitrobenzene were obtained from the corresponding anilines through diazotization, followed by a treatment with aq KI. Other iodoarenes, arenes, and solvents (dried prior to their use) as well as inorganic reagents were pure commercial products. 4-Chlorophenyl-4′-methoxyphenyliodonium chloride (**7b**)[8] and diphenyliodonium chloride (**1b**)[14] were prepared according to the reported procedures. Novel preparations of diaryliodonium iodides **1—6,a** were performed *solely* by the one-pot method reported in our previous paper;[8] their crude yields as well as their physico-chemical and ^{1}H NMR spectral characteristics are given in Tables 1 and 3. They are yellow solids, except for red-colored **4a**.

The melting points of the *purified* diaryliodonium salts listed in Tables 1 and 2 were uncorrected, and were measured as follows.[8] Since they strongly depend on the duration of heating, after an approximate mp was taken in a capillary tube, a new sample was introduced about 10 °C below this point, and the temperature was raised at a rate of 4—5 °C per minute. ^{1}H NMR spectra were recorded on a Tesla BS 567 A (100 MHz) spectrometer. Microanalyses were carried out at the Institute of Organic Chemistry, the Polish Academy of Sciences in Warsaw.

Oxidative Anion Metatheses in Diaryliodonium Iodides; General Procedure: After an appropriate *crude* diaryliodonium iodide (5 mmol) was suspended with stirring in an appropriate alcohol (10 cm^3; see Table 2), a chosen acid, HX (5.3 mmol; 6% excess), was alternatively added as follows: CF_3SO_3H (0.47 cm^3), 40% aq H_2SO_4 (1.0 cm^3), 40% aq HBF_4 (0.90 cm^3), *p*-toluenesulfonic acid monohydrate (1.0 g), or 65% aq HNO_3 (0.37 cm^3), followed by 30% aq H_2O_2 (0.35 cm^3; 3.4 mmol; 36% excess). The whole was stirred and warmed up to the boiling point, the reflux was continued until dissolving the reaction components, and then for an additional 10 min. The solution was cooled to room temperature and anhydrous Et_2O (20 cm^3; or 30 cm^3, when $HX=CF_3SO_3H$) was added with stirring. The dark reaction mixture was left overnight in a refrigerator. The precipitate was collected by filtration, washed well on the filter with anhydrous Et_2O, which removed all of the diiodine evolved in the reaction, or nearly so. After air-drying, fairly pure *crude* products were obtained in 73—94% yields. For their purification, they were dissolved in appropriate boiling solvents (Table 2) and filtered while hot if necessary; after cooling the products were precipitated out with a two-fold volume of either anhydrous Et_2O or CCl_4 (Table 2). The suspensions were left overnight in a refrigerator; the crystals were collected by filtration, washed with anhydrous Et_2O or CCl_4, and air-dried to give the *pure* iodonium salts **1—6,d—h** in 63—86% yields (Table 2). They were colorless solids, except for yellow **4g**.

Similarly, a commercial tetraethylammonium iodide was metathesized (in EtOH) into the colorless tetrafluoroborate in 95% crude yield. This was dissolved in boiling EtOH, and was precipitated out (after cooling) with a two-fold volume of Et_2O; 75% yield, mp ca. 390 °C with decomp; lit,[15] mp 365—368 °C. Found: C, 44.18; H, 9.21; N, 6.34%. Calcd for $C_8H_{20}BF_4N$: C, 44.27; H, 9.29; H, 6.45%.

Oxidative Anion Metatheses in Diaryliodonium Iodides into the Chlorides and Bromides; General Procedure: An appropriate diaryliodonium iodide (5 mmol) was suspended in MeOH (10 cm^3) acidified with HX: either 35% aq HCl (1.05 cm^3; 12 mmol; 20% excess) or 40% aq HBr (1.55 cm^3; 10.6 mmol; 6% excess). After 30% aq H_2O_2 (1.0 cm^3; 9.8 mmol; 96% excess) was added with stirring, the mixtures were refluxed for 20—30 min to remove the diiodine color. The thus-obtained hot solutions were either *yellow-colored* (HX=HCl) or *orange-colored* (HX=HBr). *Cyclohexene* (0.7 cm^3; 7 mmol; 40% excess) was added below the boiling point, and the reflux was prolonged for ca. 5 min until decoloring took place in the solutions. These were cooled to room temperature, and Et_2O (20 cm^3) was added with stirring; the suspensions were then left overnight in a refrigerator. The crystals were collected by filtration, washed well on the filter with Et_2O and air-dried; 86—92% crude yields. More soluble chloride **1b** was *quickly* recrystallized as the whole; regarding the other crude chlorides and bromides, only small analytical samples were recrystallized from MeOH *as quickly as possible*.[8)] All of the pure products, **1b,c** and **6b,c**, were colorless solids (Table 2).

Diphenyliodonium Dibromoiodate(I) (1i) from Iodide 1a: The oxidative reaction for the iodide **1a** was carried out in the presence of HX=HBr, quite similarly as above, until obtaining the said *orange-colored* solution cooled to room temperature. Et_2O (20 cm^3) precipitated out a brownish crude product. After keeping for a few h in a refrigerator, the suspension was filtered and air-dried; 86% crude yield. This was quickly recrystallized from MeOH and *immediately* filtered off after quick cooling to room temperature. After its washing on the filter with anhydrous Et_2O and air-drying, a deep-orange solid **1i** was obtained in 56% yield (Table 2). From the main filtrate (with discarding the washings) left overnight in a refrigerator, a small amount of diphenyliodonium bromide (**1c**) was filtered off and identified.

The same oxidative reaction carried out with the other diaryliodonium iodides gave only oily or semisolid, *deep-yellow* or *deep-orange colored mixtures* of dihaloiodates(I) with the respective bromides or chlorides. These mixtures may be easily converted into the bromides or chlorides in 86—92% crude yields by short (5 min) refluxing in an anhydrous MeOH admixtured with excess *cyclohexene* (Scheme 2). This procedure for converting the dihaloiodates(I) into the corresponding diaryliodonium halides (X=Br or Cl) is more effective than that offered in the literature.[6,16)] This involved chlorination of the iodides to the dichloroiodates(I) or tetrachloroiodates(III), which when dissolved in hot acetone reacted to give the iodonium chlorides.

Similarly, tetraethylammonium iodide was oxidatively converted (in EtOH/aq HBr) into the respective dibromoiodate(I) in 95% crude yield. This being *quickly* recrystallized from EtOH, gave a red-colored pure product in 76% yield; mp 125—127 °C, lit,[17)] mp 125 °C. Found: C, 24.12; H, 4.76; N, 3.37; I, 30.51%. Calcd for $C_8H_{20}Br_2IN$: C, 24.03; H, 4.83; N, 3.36; I, 30.44%.

Diphenyliodonium Chloride Complexed with 1/2 I_2 from Iodide 1a: Diphenyliodonium iodide (2.04 g; 5 mmol) was suspended in a MeOH (10 cm^3) admixtured with 36% aq HCl (0.5 cm^3; 5.6 mmol; 12% excess) and 30% aq H_2O_2 (0.35 cm^3; 3.4 mmol; 36% excess). This was warmed up to the boiling point with stirring, and the reflux (after the dissolution of the iodide) was prolonged for a further 10 min. After cooling to room temperature, a brown precipitate was collected by filtration, washed with a little MeOH, air-dried, and *quickly* recrystallized from acetonitrile; 1.24 g (56%), mp 148—150 °C (decomp), lit,[18)] mp 145—146 °C. Found: C, 32.42; H, 2.16; I, 57.16%. Calcd for $C_{12}H_{10}ClI \cdot 1/2I_2$: C, 32.50; H, 2.27; I, 57.23%.

Diphenyliodonium Triflate (1d) from Bromide 1c: *Crude* diphenyliodonium bromide (1.8 g; 5 mmol) was suspended with stirring in a boiling MeOH (10 cm^3) admixtured with CF_3SO_3H (0.53 cm^3; 6 mmol; 20% excess), *cyclohexene* (0.5 cm^3; 5 mmol; 100% excess), and 30% aq H_2O_2 (0.75 cm^3; 7.3 mmol; 192% excess). The reflux was continued to be stirred until the bromide was dissolved, and then for an additional 15 min. The solvent was distilled off under a vacuum to dryness. The residue was triturated with anhydrous Et_2O (15 cm^3), and then left overnight in a refrigerator. After filtering, the crystals were washed well on the filter with anhydrous Et_2O and dissolved in boiling *n*-PrOH; after cooling, a colorless product **1d** was precipitated out with a two-fold volume of anhydrous Et_2O. After filtering and air-drying, its properties were identical as being similar to those of the same triflate **1d**, obtained by oxidative metathesis in diphenyliodonium iodide (**1a**) (Tables 2 and 3).

Oxidative Anion Metatheses in Diaryliodonium Chlorides; General Procedure: After an appropriate *crude* diaryliodonium chloride (5 mmol) was suspended with stirring in MeOH (10 cm^3), a chosen acid, HX (6.5 mmol; 30% excess), was alternatively added as follows: 40% aq H_2SO_4 (1.2 cm^3), 40% aq HBF_4 (1.1 cm^3), or $TsOH \cdot H_2O$ (1.24 g), followed by 30% aq H_2O_2 (1.0 cm^3) and *cyclohexene* (0.5 cm^3; 5 mmol; 100% excess). The whole was stirred and refluxed for 3 h; after each hour, an additional portion (1 cm^3) of 30% aq H_2O_2 was added (the total amount of 30% aq H_2O_2 consumed: 3.0 cm^3; 29.4 mmol; 1076% excess). The solvent was distilled off under a vacuum, while removing as much H_2O as possible (it is important for the following effective purifications). The solid or oily residue was triturated either with anhydrous Me_2CO (15 cm^3; when HX=H_2SO_4 or TsOH) or with anhydrous Et_2O (15 cm^3; when HX=HBF_4), sometimes with shaking to start the crystallization. The suspensions were left overnight in a refrigerator. The crystals were collected by filtration and washed

Table 3. Exemplary Spectroscopic ^1H NMR Data of Purified Diaryliodonium Salts[a)]

Product	δ/ppm
1d	7.42—8.26 (m, 10H, ArH)
1h	2.36 (s, 3H, Me), 7.20—8.26 (m, 14H, ArH)
2d	2.38 (s, 3H, 5-Me), 2.61 (s, 3H, 2-Me), 7.44—8.15 (m, 8H, ArH)
3d	2.12 (s, 3H, COMe), 7.42—8.20 (m, 9H, ArH)
3h	2.12 (s, 3H, COMe), 2.36 (s, 3H, Me), 7.17—8.18 (m, 13H, ArH)
4f	3.96 (s, 3H, OMe), 7.20—8.68 (m, 8H, ArH)
5d	3.83 (s, 3H, OMe), 6.96—8.43 (m, 8H, ArH)
5h	2.35 (s, 3H, Me), 3.83 (s, 3H, OMe), 6.95—8.40 (m, 12H, ArH)
6d	2.38 (s, 3H, 4-Me), 2.66 (s, 3H, 2-Me), 7.09—8.36 (m, 7H, ArH)
6h	2.35[b)] (s, 6H, 4-Me), 2.64 (s, 3H, 2-Me), 7.05—8.34 (m, 11H, ArH)
7f	3.85 (s, 3H, OMe), 6.98—8.19 (m, 8H, ArH)
7h	2.36 (s, 3H, Me), 3.84 (s, 3H, OMe), 6.98—8.18 (m, 12H, ArH)

a) ^1H NMR spectra were obtained in CD_3OD at room temperature. ^1H NMR spectra of the diaryliodonium cations **1**—**7** with various counter ions are, practically, nearly the same. For the hydrogensulfates, the low-field HSO_4^- peak is absent due to a fast protium exchange with the perdeuterated solvent. For the tosylates, there are additional peaks derived from TsO^-. The same final products but obtained by the two different routes, e.g. **1d**, do exhibit the same spectra. b) ^1H NMR signals from the 4-Me groups derived from either TsO^- or $Ph(2,4\text{-}Me_2C_6H_3)I^+$ are, casually, located at 2.35 ppm.

well on the filter with either anhydrous Me_2CO or with anhydrous Et_2O, respectively. The thus-obtained crude iodonium salts **1e,f,h** and **7e,f,h** in 64—89% yields were purified quite similarly as those obtained from the metathesized diaryliodonium iodides (Table 2); the final yields of the *pure* products were 54—76% (Table 2).

These results were presented at two subsequent Meetings of the Polish Chemical Society held in Warsaw, September 12—15, 1994, and in Lublin, September 25—28, 1995. They are a part of the future dissertation of P. Kaźmierczak, M.Sc.

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10) It is also possible to steam-distill off the diiodine evolved, with leaving the metathesized iodonium salts in the remainders. This workup is, however, less effective and time-consuming.

11) Acidified (with H_2SO_4, TsOH, CF_3COOH, etc.) solutions of H_2O_2 have been applied[9] for *aromatic iodination* of activated arenes, hence the assumed transient iodine(I) species, such as $I{-}\overset{+}{O}H_2$ or AcOI, would react in the iodinating solutions. The equation (a) is possibly obeyed when e.g. KI was used as the oxidized iodinating agent. When diiodine is used for the oxidative iodination, the following pathway is possible: $H_2O_2+I_2\longrightarrow 2I{-}OH\xrightarrow{2H^+}2I{-}\overset{+}{O}H_2$. Similar pathways (a) and (b) are very likely encountered in the oxidative metatheses of diaryliodonium bromides and chlorides into the other salts.

12) It is known that both diaryliodonium and tetraalkylammonium iodides are easily converted into the respective dihaloiodates(I) either by the reaction of dichlorine or dibromine with iodides, or by the reaction of IBr or ICl with the corresponding bromides or chlorides. For more details see Ref. 3, Chap. 7.

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