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Iodination and Chlorination of Aromatic Polycyclic Hydrocarbons with Iodine Monochloride in Aqueous Sulfuric Acid*

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Abstract—Polycyclic aromatic hydrocarbons when treated with iodine monochloride in water solutions of sulfuric acid afford iodo- and chloroderivatives. Biphenyl, fluorene, acenaphthene, 1-nitronaphthalene undergo iodination. Naphthalene furnishes a mixture of iodo- and chloroderivatives, prevailing the latter. Anthracene and phenanthrene provide only chlorinated products. The iodine monochloride in the sulfuric acid is a stronger iodinating agent than in acetonitrile.

Polycyclic hydrocarbons readily undergo electrophilic substitution but at the same time they are the most prone among the other aromatic compounds to many side and undesired processes. It is specifically true for iodination reaction. In common iodinating systems containing oxidant these substrates form charge-transfer complexes with iodine that prevent iodination. In some cases the formation of these complexes is avoided by addition of electron-donor compounds [1, 2]. In concentrated acid solutions the polycyclic arenes are protonated, and in reactions with electrophiles very often occurs one-electron transfer [3]; in both cases arise very reactive species, ion-radicals, that further undergo undesired transformations.

We showed in [4, 5] that iodine monochloride in aqueous sulfuric acid was a sufficiently versatile iodinating agent that iodinated both electron-rich aromatic compounds (aniline, aromatic nitroamines, phenol ethers, alkylbenzenes) and moderately deactivated arenes (halobenzenes, aromatic carboxylic acids, some nitroarenes). Therewith the activity of the electrophilic iodine and the preparative yields of the reaction products can be controlled by the concentration of sulfuric acid: the more active is the arene in electrophilic substitution processes, the lower is the acid concentration required for iodination. The control of the acid concentration also helps to avoid many side processes.

We report here on the results of investigations concerning iodine monochloride reactions with polycyclic aromatic hydrocarbons: fluorene **Ia**, biphenyl **IIa**, acenaphthene **IIIa**, anthracene **IVa**, phenanthrene **Va**, naphthalene **VIa**, 1-nitronaphthalene **VIIa** in water solutions of sulfuric acid.

The use of H_2SO_4 of low concentration (10–30 vol%) ensures a minimum of side reactions. Preliminary experiments and results of the preceding work [4, 5] showed that at a higher H_2SO_4 concentration arenes active in the electrophilic processes predominantly entered into side reactions resulting in considerable tarring. We found experimentally that the fullest conversion of the original compounds into monohalogenated products was achieved at the use of 1.5–2 equiv. of iodine monochloride.

We established that polycyclic hydrocarbons rather easily underwent halogenation by ICl in sulfuric acid solutions but the pattern of their behavior was individual (Table 1).

With fair preparative yields were obtained mono- and diiododerivatives of compounds **Ia–IIIa**: 2-iodofluorene (**Ib**) and 2,7-diiodofluorene (**Ic**); 4-iodobiphenyl (**IIb**), 4,4–diiododibiphenyl (**IIc**) and 5-iodoacenaphthene (**IIIb**). Naphthalene **VIa** affords quite a number of compounds, both iodinated and chlorinated, but we did not try to isolate them since the similar values of R_f suggested that chromatographic separation was not promising. Nitronaphthalene **VIIa** did not undergo iodination in sulfuric acid of 10–50% concentration, but as we had reported earlier [4] 1-iodo-5-nitronaphthalene had been obtained therefrom in 21% preparative yield in 90% sulfuric acid.

Table 1. Reaction of polycyclic aromatic compounds with iodine monochloride in water solutions of sulfuric acid

Substrate	Ratio substrate: reagent, mmol	Concn. H_2SO_4, vol%	Temperature, °C	Time, h	Reaction product	Yield, %	mp, °C (solvent)	Publ. mp, °C
Fluorene (**Ia**)	10:15	10	100	2	2-Iodofluorene (**Ib**)	32	125–126 (2-propanol)	126–127 [12]
	10:30	10	100	2	2,7-Diiodofluorene (**Ic**)	43	211–213 (2-propanol)	213–214 [11]
Biphenyl (**IIa**)	10:15	10	100	3	4-Iodobiphenyl (**IIb**)	23	112–113 (ethanol)	113–114 [10]
	10:30	10	100	3	4,4'-Diiodobiphenyl (**IIc**)	35	202–204 (ethanol)	204 [11]
Acenaphthene (**IIIa**)	10:20	5	100	2	5-Iodoacenaphthene (**IIIb**)	49	59–61 (hexane)	63–65.5 [12]
Anthracene (**IVa**)	10:20	10	100	3	9-Chloroanthracene (**IVb**)	65	102–103 (ethanol)	103 [10]
	10:40	10	100	3	9,10-Dichloroanthracene (**IVc**)	37	209–210 (ethanol)	209–210 [10]
Phenanthrene (**Va**)	10:30	10	100	3	9-Chlorophenanthrene (**Vb**)	30	52–53 (ethanol)	53–53.5 [10]

Anthracene **IVa** and phenanthrene **Va** in reaction with iodine monochloride gave rise exclusively to chloroderivatives. Therewith anthracene **IVa** depending on the reagents ratio afforded both 9-chloro (**Vb**) and 9,10-dichloroanthracene (**IVc**). In order to direct the process with anthracene to iodination we attempted to effect an additional heterolysis of the I–Cl bond along a hypothetical scheme.

Scheme.

$$ICl + H_2O \rightarrow IOH + HCl$$

$$IOH + H^+ \rightarrow IO^+H_2$$

$$IO^+H_2 \rightarrow I^+ + H_2O$$
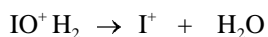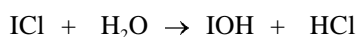
To this end the iodine monochloride was stirred for 4 h in 10, 50, or 90% H_2SO_4 at room temperature or at 100°C, and anthracene was charged into the reaction mixture afterwards. However this procedure did not afford any iodinated products.

Phenanthrene (**Va**) as anthracene (**IVa**) also underwent only chlorination. It turned out to be the least active among the compounds under study. We did not succeeded to convert it fully into halogenated product at 90–100°C in 10, 30, and 50% solutions of sulfuric acid. Even at fourfold excess of iodine monochloride and reaction at 90–100°C after 6 h TLC test still revealed the presence of the original compound **Va**.

The halogenated reaction product (mp 42–42°C) separated from the initial substrate **Va** was a mixture of chloro-substituted phenanthrenes. The main product, 9-chlorophenanthrene (**Vb**), was isolated from the products mixture by recrystallization from ethanol.

To estimate in more detail the effect of arene **Ia, IIIa–VIa** structure on the ratio of iodinated and chlorinated products we analyzed the mixtures of products obtained under conditions of kinetically controlled reaction by GC-MS method. In these experiments in contrast to preparative runs we used equimolar ratio of ICl and arenes in question, and the reactions were stopped at early conversion stages (save the case of phenanthrene **Va**) (Table 2). In the latter case the GC-MS analysis was carried out on a sample of halophenanthrenes obtained in the preparative synthesis at iodination of substrate **Va** with the threefold excess of iodine monochloride and separated from he original compound by chromatography.

By the fluorene (**Ia**) example we established that on raising the reaction temperature from 20 to 100°C selectivity of iodination is reduced as expected (at 100°C was formed ~4% of 2,7-diiodofluorene). Besides it should be noted that the isomeric chloro-fluorenes were not detected in the reaction products obtained at room temperature but appeared in the reaction mixture only at elevated temperature. In

Table 2. Composition of reaction products of polycyclic arenes **Ia, IIIa–VIa** with iodine monochloride in 10% sulfuric acid

Substrate (temperature, °C)	$E_{1/2}$, V [6]	Reaction product	Content of the main substance, %	Mass spectrum, m/z (I_{rel}, %)
Fluorene (**Ia**) (20)	1.25	Fluorene	59	166 $[M]^+$ (100), 139 (7), 115 (4), 82 (14), 69 (6), 63 (3)
		2-Iodofluorene	41	292 $[M]^+$ (66), 165 (100), 139 (3.5), 127 (3), 115 (3), 82 (15), 63 (4)
Fluorene (**Ia**) (100)	1.25	Fluorene	34.5	166 $[M]^+$ (100), 139 (7), 115 (4), 82 (14), 69 (6), 63 (3)
		2-Iodofluorene	59.5	292 $[M]^+$ (66), 165 (100), 139 (3.5), 127 (3), 115 (3), 82 (15), 63 (4)
		2,7-Diiodofluorene	3.9	418 $[M]^+$ (100), 291 (68), 209 (11), 163 (77), 145 (20), 127 (7), 98 (4), 82 (27), 63 (6), 32 (4)
		2-Chlorofluorene	1.1	200 $[M]^+$ (27), 166 (100), 163 (17), 139 (3), 82 (14)
Naphthalene (**VIa**) (100)	1.34	Naphthalene	10.8	128 $[M]^+$ (100), 102 (7), 74 (2), 64 (3), 51 (3)
		1-Iodonaphthalene	13.1	254 $[M]^+$ (100), 127 (88), 101 (5), 77 (5), 63 (3), 51 (3)
		1-Chloronaphthalene	69.9	166 $[M]^+$ (33), 162 (100), 127 (31), 126 (14), 81 (8), 63 (9), 50 (3)
		2-Chloronaphthalene	5.1	162 $[M]^+$ (100), 127 (31), 126 (14), 81 (8), 63 (9), 50 (3)
		Isomeric dichloronaphthalenes	1.1	200 $[M]^+$ (70), 196 (100), 161 (20), 160 (7), 126 (24), 122 (9), 99 (14), 74 (8), 63 (7)
Acenaphthene (**IIIa**) (100)	1.11	Acenaphthene	60.6	153 $[M]^+$ (100), 126 (4), 76 (22), 63 (6)
		3-Iodoacenaphthene	6.9	280 $[M]^+$ (100), 152 (71), 126 (8), 78 (10), 63 (6)
		5-Iodoacenaphthene	31.3	280 $[M]^+$ (100), 152 (71), 126 (8), 76 (9), 63 (6)
		5-Chloroacenaphthene	1.1	188 $[M]^+$ (56), 153 (100), 94 (6), 76 (20), 44 (9)
Anthracene (**IVa**) (100)	0.84	Anthracene	21	178 $[M]^+$ (100), 152 (10), 88 (10), 76 (7)
		9-Chloroanthracene	63	212 $[M]^+$ (100), 176 (33), 151 (9), 121 (4), 106 (9), 93 (9), 88 (24), 75 (9)
		9,10-Dichloroanthracene	16	246 $[M]^+$ (100), 211 (7), 176 (38), 123 (17), 105 (9), 87 (12), 75 (4)
Phenanthrene (**Va**) (100)	1.23	9-Chlorophenanthrene	95.3	212 $[M]^+$ (100), 176 (38), 151 (7), 106 (10), 93 (8), 88 (25), 75 (10)
		Isomeric dichlorophenanthrenes	4.7	246 $[M]^+$ (100), 210 (7), 176 (35), 123 (14), 105 (9), 88 (14), 74 (4)

general the chlorinated products either were absent or were obtained in minor amounts (~1%) with fluorene (**Ia**) and acenaphthene (**IIIa**). With naphthalene (**VIa**) arise more chlorinated than iodinated products, and anthracene (**IVa**) and phenanthrene (**Va**) afford no iododerivatives (Table 2).

It is known [3] that in reaction with iodine monochloride in acetonitrile some polycyclic hydrocarbons characterized by half-wave oxidation potential $E_{1/2} < 1.58$ V afford exclusively chloroderivatives, and 1-nitronaphthalene does not react with ICl in acetonitrile. Our results show that iodinating ability of ICl in the sulfuric acid is notably higher than in acetonitrile. Also the fraction of iodinated products as compared to that of chloroderivatives is also higher in

sulfuric acid indicating that iodination is more selective. In this medium are iodinated fluorene **Ia**, biphenyl (**IIa**) ($E_{1/2} < 1.48$ V), acenaphthene (**IIIa**), naphthalene (**VIa**) that have $E_{1/2}$ values considerably lower than 1.58 V, and 1-nitronaphthalene (**VIIa**) which is inert in acetonitrile [4]. Besides, acenaphthene (**IIIa**) possessing lower value of $E_{1/2}$ than polycycles **Va** and **VIa** provides considerably less of chlorination product (Table 2). Thus the value of half-wave potential 1.58 V assumed in [3] as criterion of iodination possibility of polycyclic hydrocarbons with iodine monochloride cannot be considered as generally valid. Our results are not in disagreement with the mechanism of iodination and chlorination of polycyclic hydrocarbons by ICl suggested in [3]: It is presumed that aromatic cation-radicals arise which

further undergo recombination with iodine radical and chloride anion. It should be noted that numerous other iodinating reagents are the most active in sulfuric acid medium (see, e.g., [7–9]).

EXPERIMENTAL

The reaction process was monitored and the purity of the compounds obtained was checked by TLC on Silufol UV-254 plates, eluent hexane, development under UV irradiation. ^{1}H NMR spectra were registered on spectrometer Tesla BS-497 (100 MHz) in $CDCl_3$. GC-MS analyses were performed on HP 5972 and HP 5890 instruments (electron impact, 70 eV, quartz capillary column HP-5, 30 m × 0.25 mm, stationary phase copolymer of 95% of dimethylsiloxane and 5% of diphenylsiloxane, 0.25 μ thick). Iodine monochloride from ICN Pharmaceuticals Inc. was used without additional purification, the other substrates and reagents were of "chemically pure" grade. The structures of iodination products were determined from comparison of their spectral characteristics, analyses, and melting points with authentic samples.

Halogenation of polycyclic hydrocarbons. In the experiments for GC-MS analysis of products compositions to 10 mmol of iodine monochloride in 40 ml of water solution of H_2SO_4 was added at stirring 10 mmol of aromatic substrate **Ia–VIa**, the mixture was heated to 100°C, and stirred for 3 h. The reaction mixture was poured into water and washed with sodiumcarbonate solution. The solid products obtained from halogenation of compounds **Ia–Va** were filtered off, dried, dissolved in CCl_4, purified from tars on a short column packed with Al_2O_3, and analyzed. The liquid halogen-containing products arising in reaction with naphthalene **VIa** were extracted with hexane, dried on $CaCl_2$, and purified on a short column packed with Al_2O_3. Similarly were carried out the preparative syntheses of haloderiv-

atives of polycyclic hydrocarbons and isolation of the reaction products **Ib, c, IIb, c, IIIb, IVb, c, Vb**. The recrystallization of the products was performed from the solvents indicated in Table 1.

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