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Abstract

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PREPARATION OF ARYL HALIDES FROM AROMATIC HYDROXY COMPOUNDS

The simplest method for preparing aryl halides is the direct halogenation of aromatic hydrocarbons (ArH). However, this method has two substantial shortcomings, namely: the limited scope of its application and the occurrence of halogenation in several directions. For example, β-halonaphthalene, m-halotoluene, and o-halobiphenyl can practically not be obtained at all by direct halogenation of arenes (ArH), whereas all aryl halides obtained in this way (with the sole exception of halobenzenes) are mixtures of the corresponding positional isomers (usually with one of them predominating), the separation of which, because of the closeness of their boiling points, presents considerable difficulties. Thus, the α-halonaphthalenes obtained by halogenation of naphthalene can be freed from the constantly formed admixture of β-isomers (content up to 5-10%) only by repeated crystallization of the halogenation product from absolute ethanol or another solvent at a temperature of -15 to $-20°$ ($^{1-3}$). The preparation of aryl halides by the Sandmeyer reaction, although it is a universal method, is distinguished by the considerable complexity of preparing the starting amines and has a number of other disadvantages.

Meanwhile, aromatic hydroxy compounds, such as naphthols, cresols, o-hydroxybiphenyl, and others, are readily available industrial products, and most of them are stable crystalline substances, the purification and accurate assessment of the degree of purity of which are extremely simple. Therefore, of particular interest is the method proposed in 1957 by English chemists (^{4}) for obtaining aryl halides ArX from the corresponding hydroxy compounds ArOH and phosphorus pentachloride according to the following multistage scheme:

$$3\mathrm{Ar'OH} + \mathrm{PCl_5} \xrightarrow{120-140^\circ} (\mathrm{Ar'O})_3\mathrm{PCl_2} + 3\mathrm{HCl};$$

$$(\mathrm{Ar'O})_3\mathrm{PCl_2} + \mathrm{ArOH} \xrightarrow{120-140^\circ} (\mathrm{Ar'O})_3(\mathrm{ArO})\mathrm{PCl} + \mathrm{HCl};$$

$$(\mathrm{Ar'O})_3(\mathrm{ArO})\mathrm{PCl} \xrightarrow{250-350^\circ} \mathrm{ArCl} + (\mathrm{Ar'O})_3\mathrm{PO},$$

where $\mathrm{Ar}'\mathrm{OH}$ is an aromatic hydroxy compound possessing greater electron-donor properties than ArOH (phenol, *p*-cresol, or, best of all, *p*-tert-butylphenol).

For the preparation of aryl bromides (ArBr) or aryl iodides (ArJ), the compound $(\mathrm{Ar}'\mathrm{O})_3(\mathrm{ArO})\mathrm{PCl}$, before being pyrolyzed, is boiled with an excess of $\mathrm{C_2H_5Br}$ or $\mathrm{CH_3J}$, for example:

$$(\mathrm{Ar}'\mathrm{O})_3(\mathrm{ArO})\mathrm{PCl} + \mathrm{C_2H_5Br} \xrightarrow{t} (\mathrm{Ar}'\mathrm{O})_3(\mathrm{ArO})\mathrm{PBr} + \mathrm{C_2H_5Cl};$$

$$(\mathrm{Ar}'\mathrm{O})_3(\mathrm{ArO})\mathrm{PBr} \xrightarrow{250-350^{\circ}} \mathrm{ArBr} + (\mathrm{Ar}'\mathrm{O})_3\mathrm{PO}.$$

However, under the stated conditions, despite the high electron-donating ability of $Ar'OH$, pyrolysis of the reaction products always also gives the undesirable halide $Ar'X$:

$$(Ar'O)_3(ArO)PX \xrightarrow{250—350^{\circ}} Ar'X + (Ar'O)_2(ArO)PO,$$

where the yields of $Ar'X$ reach 70% for $Ar' = C_6H_5$ and 50-55% for Ar'-*p*-tert-$C_4H_9C_6H_4$. Thus, for example, even when $Ar' = p$-tert-$C_4H_9C_6H_4$, the yield of β-chloronaphthalene was 65%, that of its α-isomer 60% (^{4}), while that of *o*-chlorobiphenyl, as we have shown, was only $\sim$ 50%.

Aryl bromides ($ArBr$) are formed in still lower yields, since the reaction of chlorine-bromine exchange in the compound $(Ar'O)_3(ArO)PCl$, naturally, does not proceed quantitatively, and the pyrolysis products already contain four different halides ($ArBr$ and $ArCl$, $Ar'Br$ and $Ar'Cl$), which, of course, not only lowers the yield of $ArBr$ but also complicates its isolation and purification. Thus, if p-ClC_6H_4Cl from p-ClC_6H_4OH and p-$CH_3C_6H_4Cl$ from p-$CH_3C_6H_4OH$ were obtained in yields of 71 and 87%, respectively, then the yield of the corresponding bromides was only 45 and 51% (^{4}). In this way we succeeded in obtaining *o*-bromobiphenyl in a yield of only 25-30% (the yield of *o*-chlorobiphenyl $\sim$ 50%).

The shortcomings indicated served as the impetus for developing a modified procedure for the synthesis of individual aryl halides ArX, starting only from the corresponding hydroxy compounds $ArOH$ and PX_5. It was found that replacement of the hydroxy group in $ArOH$ by chlorine, with the aim of obtaining $ArCl$, can be carried out in one stage by heating the corresponding aromatic hydroxy compound with phosphorus pentachloride, in a molar ratio of 4 : 1, at 140—160°, for 3-5 hr, followed by pyrolytic decomposition of the resulting chlorotetraaryloxyphosphorus at 280—300°:

$$4ArOH + PCl_5 \xrightarrow{140—160^{\circ}} (ArO)_4PCl + 4HCl;$$

$$(ArO)_4PCl \xrightarrow{280—300^{\circ}} ArCl + (ArO)_3PO,$$

and the yields of aryl chlorides here, irrespective of the electron-donating ability of the initial $ArOH$, are almost theoretical (92-95%).

In a similar manner, starting from $ArOH$ and PBr_5 (molar ratio 4 : 1), we prepared a series of individual aryl bromides $ArBr$, the yields being 70–95% of theory:

$$4ArOH + PBr_5 \xrightarrow{130—140^{\circ}} (ArO)_4PBr + 4HBr;$$

$$(ArO)_4PBr \xrightarrow{250—280^{\circ}} ArBr + (ArO)_3PO.$$

This modification of the reaction made it possible completely to eliminate the formation of side aryl halides contaminating ArX; to shorten the duration of the process considerably (by a factor of 2–5) and to increase the yields of aryl halides by a factor of 1.5–2. The use of some excess $ArOH$ relative to the stoichiometric ratio does not reduce the yield of ArX and does not complicate its purification, since the $ArOH$ impurity can readily be removed by treating the reaction products with alkali. An advantage of this method also lies in the fact that the triaryl phosphates $(ArO)_4PX$ formed during pyrolysis can, by 5-8 hr heating with alkali, be partially ($\sim$ by $^2/_3$) hydrolyzed, and the hydroxy compounds $ArOH$ isolated thereby, without any special purification, can again be used for obtaining aryl halides from them. Hydrolysis of mixed phosphates $(Ar'O)_2(ArO)PO$, or of their mixtures with $(Ar'O)_3PO$, formed under the conditions (^{4}), inevitably leads to a difficultly separable mixture of two hydroxy compounds–$Ar'OH$ and $ArOH$.

For the preparation of halonaphthalenes we used previously dried naphthols of chemically pure grade. The initial *o*-hydroxybiphenyl was isolated by 2–3-fold vacuum fractionation of the distillation residue from the production of phenol by the method of alkaline fusion (sometimes with subsequent recrystallization from petroleum ether), b.p. 89-91° (1 mm), m.p. 54-56°; according to (5), m.p. 58°. Phosphorus pentabromide was prepared immediately before the experiments by brominating PBr_3 with bromine in an inert solvent ($CHCl_3$, CH_2Cl_2).

Preparation of aryl chlorides. Into a flask equipped with a stirrer, a reflux condenser, and a thermometer, under nitrogen, were introduced 125 g (0.6 mole) of phosphorus pentachloride and 346 g (2.4 moles) of dry β-naphthol. The mixture was stirred at 140–145° for 5 hr, after which it was pyrolyzed for 15–20 min at 300°. Distillation of the pyrolysis products under vacuum gave 92.5 g (95%) of β-chloronaphthalene, m.p. 55-56° (from 96% ethanol). A mixed-melting-point test of the latter with a sample of β-chloronaphthalene obtained by isomerization of α-chloronaphthalene over an aluminosilicate catalyst showed no depression of the melting point. Reducing the heating time of the mixture of β-$C_{10}H_7OH$ and PCl_5 from 5 to 3 hr scarcely changed the yield of β-chloronaphthalene (92%). α-Chloronaphthalene and *o*-chlorobiphenyl were obtained analogously.

Preparation of aryl bromides. To 49.5 ml (0.52 mole) of PBr_3 in 100 ml of $CHCl_3$ was added dropwise a solution of 27.7 ml (0.54 mole) of bromine in 100 ml of $CHCl_3$ (temperature of the reaction mixture from −15 to −5°; 4.5 hr; stirring). To the PBr_5 formed as a yellow precipitate was added, at room—

Table 1

Initial Ar in ArOH	ArCl: yield, %	ArCl: b.p., °C (mm)	ArCl: m.p., °C	ArCl: Cl content, %, found	ArCl: Cl content, %, calc.	ArCl: literature data (°)	ArBr: yield, %	ArBr: b.p., °C (mm)	ArBr: n_D^{20}	ArBr: d_4^{20}	ArBr: Br content, %, found	ArBr: Br content, %, calc.	ArBr: literature data (°)
m-$CH_3C_6H_4$	—	—	—	—	—	—	70	180.5–182 (751)	1.5528	1.4106	46.98	46.72	b.p. 184–184.1° (754.1 mm); d_4^{20} 1.4099
α-$C_{10}H_7$	93*	112.5—113 (4)		21.51	21.84	b.p. 262.7° (760 mm); n_D^{20} 1.6332; d_4^{20} 1.1938	87	140–140.5 (13)	1.6580	1.4830	38.64	38.60	b.p. 281.1° (760 mm); n_D^{20} 1.6582; d_4^{20} 1.4834
β-$C_{10}H_7$	92–95	263–265 (760)	55–56	21.63	21.84	b.p. 421–422° (12 mm); m.p. 58°	93.5**	162–163.5 (8.5)	—	—	38.04	38.60	b.p. 281–282° (760 mm); m.p. 58–59°

Initial Ar in ArOH	ArCl: yield, %	ArCl: b.p., °C (mm)	ArCl: m.p., °C	ArCl: Cl content, %, found	ArCl: Cl content, %, calc.	ArCl: literature data (°)	ArBr: yield, %	ArBr: b.p., °C (mm)	ArBr: n_D^{20}	ArBr: d_4^{20}	ArBr: Br content, %, found	ArBr: Br content, %, calc.	ArBr: literature data (°)
o-$C_6H_5C_6H_4$	92.5	98–98.5 (2.5)	31–32	19.06 18.87	19.23	b.p. 267–268° (760 mm); m.p. 34°	79	90–91.5 (1.5)	1.6243	1.2766	34.02 33.95	34.29	b.p. 160° (11 mm); d_{20}^{20} 1.2175

* n_D^{20} 1.6335; d_4^{20} 1.1937.
** M.p. 56.5-57° (from ethanol).

at room temperature dropwise over 2 hr 216 g (2 moles) of *m*-cresol, after which the solvent was distilled off, the mixture was heated at 130° until the evolution of HBr ceased (2 hours), and then pyrolyzed for 30 min at 280°. By distillation of the pyrolysis products, *m*-bromotoluene was isolated; after treatment with an aqueous alkali solution it was redistilled, yield 59.5 g (70%). The synthesis of other aryl bromides was carried out in a similar manner, but for a shorter time.

The properties and elemental-analysis data of the aromatic chlorides and bromides obtained by us are given in Table 1.

Hydrolysis of triaryl phosphates. A mixture of 17 g (0.036 mole) of $(\beta-C_{10}H_7O)_3PO$ and 18.3 g (0.321 mole) of KOH in 50 ml of water was stirred at 100-105° for 5 hr, then treated with 150 ml of 10% HCl. The white precipitate that separated was filtered off, washed with water, and dissolved in 120 ml of ether. The ethereal solution was dried over Na_2SO_4, the ether was distilled off, and the residue was distilled in vacuo. 10 g (65% of theory) of β-naphthol was obtained, b.p. 141-143° (10 mm), m.p. 120-121°. A mixed-melting-point test with an authentic sample of β-naphthol showed no depression. The literature[6] gives for β-naphthol b.p. 285-286°, m.p. 122°.

The hydrolysis of $(\alpha-C_{10}H_7O)_3PO$ was carried out by us in a similar manner; yield of α-naphthol 9.3 g (60%). According to the data of[8], alkaline hydrolysis of $(C_6H_5O)_3PO$ under the action of an excess of 1 *N* NaOH at 85° also proceeds only to about 2/3 (phenol yield 63%).

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Note: Figure translations are in progress. See original paper for figures.