# Palladium-Catalyzed Hydrodehalogenation of Haloaromatic Compounds

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The reductive dehalogenation (hydrodehalogenation) of aromatic *C*-halo compounds has extensive synthetic applications. In general, palladium and its compounds are used for this hydrodehalogenation[1-5]. We report here a new simple method for the hydrodehalogenation of aryl chlorides, bromides, and iodides in high yield by heating these aryl halides in formic acid/dimethylformamide in the presence of a catalytic amount of palladium-on-carbon.

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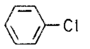
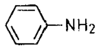
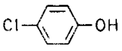
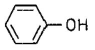
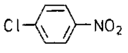
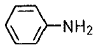
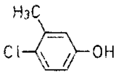
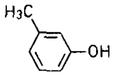
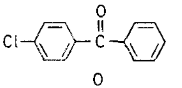
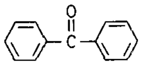
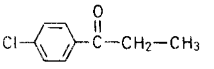
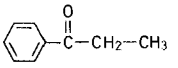
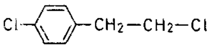
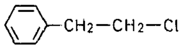
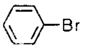
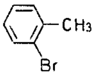
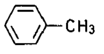
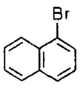
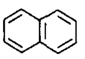
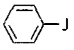
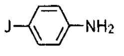
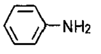
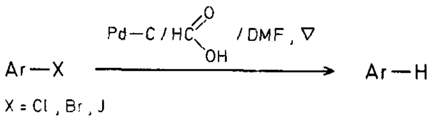
**Table.** Hydrodehalogenation of Aryl Halides with Palladium-on-Carbon in Formic Acid/Dimethylformamide

| Educt | | Product | Molar ratio Pd : Educt | Reaction time [h] | Yield [%] | m.p. [°C] or b.p. [°C]/760 torr | |
|---|---|---|---|---|---|---|---|
| | | | | | | found | reported[6] |
|  | ⟶ |  | 0.026 | 4[a] | 85-90 | b.p. 80° | b.p. 80.1° |
|  | ⟶ |  | 0.030 | 3[a] | 90-95 | b.p. 183-184° | b.p. 184.13° |
|  | ⟶ |  | 0.030 | 5[b] | 80-85 | m.p. 42-43° | m.p. 43° |
|  | ⟶ |  | 0.037 | 3[a] | 85-90 | b.p. 184° | b.p. 184.13° |
|  | ⟶ |  | 0.034 | 5[b] | 85-90 | b.p. 200-202° | b.p. 202.2° |
|  | ⟶ |  | 0.051 | 5[b] | 80-85 | m.p. 47-48° | m.p. 48.1° |
|  | ⟶ |  | 0.040 | 6[b] | 80-85 | m.p. 18° | m.p. 18.61° |
|  | ⟶ |  | 0.052 | 5[b] | 80-85 | b.p. 196-197° | b.p. 197-198° |
|  | ⟶ |  | 0.037 | 3[a] | 85-90 | b.p. 80° | b.p. 80.1° |
|  | ⟶ |  | 0.040 | 3[a] | 80-85 | b.p. 110-111° | b.p. 110.6° |
|  | ⟶ |  | 0.049 | 3[b] | 80-85 | m.p. 79-80° | m.p. 80.55° |
|  | ⟶ |  | 0.048 | 2[a] | 90-95 | b.p. 80° | b.p. 80.1° |
|  | ⟶ |  | 0.052 | 2[a] | 90-95 | b.p. 184° | b.p. 184.13° |

[a] The reactions were monitored by G.L.C. and were terminated after the starting halo compounds had been consumed.

[b] Completion of the reaction was determined by T.L.C.



$$\mathrm{Ar{-}X} \xrightarrow{\mathrm{Pd{-}C\,/\,HCOOH\,/\,DMF,\ \nabla}} \mathrm{Ar{-}H}$$

X = Cl, Br, J

The hydrodehalogenation can also be achieved by refluxing haloaromatic compounds in formic acid alone in presence of palladium, but it was observed that the reaction rate is very slow. To assess the function of dimethylformamide as reducing agent the reaction was carried in the absence of formic acid; hydrodehalogenation does not take place under these conditions.

In the case of halonitroarenes, the nitro group is reduced to an amino group in the reaction. Other functional groups present such as ketonic carbonyl groups remain unaffected. Fluorobenzenes are not hydrodefluorinated by our method; thus, under the conditions used by us 4-fluoronitrobenzene is reduced to 4-fluoroaniline (20 h at reflux temperature). Aliphatic *C*-halo compounds do not undergo the hydrodehalogenation described here; thus, chlorocyclohexane remains unaffected. Chloroalkylchloroarenes are selectively hydrodechlorinated at the aromatic ring.

The use of easily available reagents, the simple performance, and the high yields render our method advantageous over other methods for the same purpose[1]. The only costly reagent, 5% or 10% palladium-on-carbon, is used in catalytic amounts and may be recovered with only little loss in activity.

**Hydrodebromination of 1-Bromonaphthalene; Typical Procedure:**

1-Bromonaphthalene (2 g, 9.7 mmol) is dissolved in formic acid (85%, 5 ml) + dimethylformamide (25 ml), 10% palladium-on-carbon (0.5 g, 0.47 mmol) is added, and the mixture is refluxed for 3 h. T.L.C. analysis (5% silver nitrate/silica gel, hexane as solvent) then shows completion of the reaction. The mixture is cooled, the catalyst is filtered off and washed with benzene, and the filtrate is diluted with water (50 ml) and extracted with benzene (3 × 25 ml). The combined organic layer is washed with water (50 ml), 10% sodium hydrogen carbonate solution (50 ml), and saturated sodium chloride solution (20 ml). The solvent is removed and the residual crude product (1.2 g) purified by sublimation to give white flakes of *naphthalene*; yield: 1.0 g (81%); m.p. 79-80 °C (Ref.[6], m.p. 80.55 °C).

The analogous reactions with halobenzenes and their simple derivatives were carried out on 10-20 g scales. After removal of the catalyst, the products were isolated by fractional distillation.

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[1] P. Helquist, *Tetrahedron Lett.* **1978,** 1913; and references cited therein.

[2] W. L. Mosby, *J. Org. Chem.* **24,** 421 (1959).

[3] B. A. Fox, T. L. Threlfall, *Org. Synth. Coll. Vol.* V, 346 (1973).

[4] I. D. Entwistle, R. A. W. Johnstone, T. J. Povall, *J. Chem. Soc. Perkin Trans. 1* **1975,** 1300.

[5] G. D. Pandey, K. P. Tiwari, *Synth. Commun.* **1980,** 523.

[6] *Handbook of Chemistry and Physics*, 58th Edn., The Chemical Rubber Co., Cleveland, Ohio, 1977–1978.

0039-7881/82/1032-0878 $ 03.00