PALLADIUM HYDRIDES IN ORGANIC SYNTHESIS. REDUCTION OF ARYL BROMIDES

BY SODIUM FORMATE CATALYZED BY TETRAKIS(TRIPHENYLPHOSPHINE)PALLADIUM
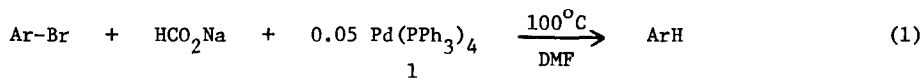
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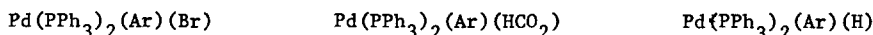
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Earlier we reported a new method for the reduction of aryl halides to arenes with sodium methoxide as a source of hydride and tetrakis(triphenylphosphine)palladium (1) as a catalyst.[1] However, an alternative source of hydride for this reduction is conceivably sodium formate which has previously been employed in a few transition metal-promoted reductions.[2] Formate is a very attractive hydride donor because of its ease of handling, low cost, and mildness as a reagent.

We are now pleased to report that the use of sodium formate in place of sodium methoxide results in a major improvement in our method for the reduction of aryl halides. This communication is prompted in part by Heck's very recent use of triethylammonium formate in a similar reaction.[3] In our new procedure, aryl bromides react at 100°C with sodium formate in the presence of a catalytic amount of 1 with N,N-dimethyl formamide (DMF) as the solvent (equation 1). Typical results are given in the table. A minor by-product in all cases, as in our earlier report, is benzene which presumably arises from cleavage of triphenylphosphine.[1]

$$\text{Ar-Br} \quad + \quad \text{HCO}_2\text{Na} \quad + \quad 0.05 \text{ Pd(PPh}_3)_4 \quad \xrightarrow[\text{DMF}]{100°\text{C}} \quad \text{ArH} \tag{1}$$
$$\underline{1}$$

In comparison to our earlier procedure, the present method is a far more generally useful reaction, because of its excellent functional group compatibility (see runs 6-10) which apparently is a result of the much lower basicity of formate compared to methoxide. Even the very sensitive aldehyde group survives the reaction (run 6). A number of other methods have been developed for the reduction of aryl halides,[4] including the use of catalytic hydrogenolysis, Raney nickel, and lithium aluminum hydride, but these methods are incompatible with several functional groups.

The mechanism of the reaction most likely involves oxidative addition[5] of the aryl bromide to a coordinatively unsaturated palladium complex to give 2 which then undergoes metathetical replacement of bromide by formate to produce 3. Loss of carbon dioxide from 3 generates the palladium hydride (4) from which the arene and a catalytically active palladium species are formed by reductive elimination. In our earlier work with methoxide,[1]

$$\text{Pd(PPh}_3)_2(\text{Ar})(\text{Br}) \qquad\qquad \text{Pd(PPh}_3)_2(\text{Ar})(\text{HCO}_2) \qquad\qquad \text{Pd(PPh}_3)_2(\text{Ar})(\text{H})$$
$$\underline{2} \qquad\qquad\qquad\qquad \underline{3} \qquad\qquad\qquad\qquad \underline{4}$$

Reduction of Aryl Bromides[a]

Run	Aryl Bromide	Conversion (%)	Yield of ArH (%)[b]
1	2-Bromonaphthalene	100	82 (79)[c]
2	4-Bromobiphenyl	98	81
3	4-Bromotoluene	100	62
4	Bromobenzene	100	105[d]
5	4-Bromophenyl Phenyl Ether	100	65
6	4-Bromobenzaldehyde	90	80
7	4-Bromoacetophenone	89	84
8	Methyl 3-Bromobenzoate	91	84
9	3-Bromobenzoic Acid	100	48
10	2-Bromonitrobenzene	74	65

[a] All reactions were performed with 1.5 equiv. of sodium formate and 0.05 equiv. of 1 at 100°C for 6 hr. [b] Unless otherwise noted, yields were determined by glpc analysis with an internal standard. Yields were not optimized. [c] Isolated yield. [d] Includes benzene produced presumably by cleavage of triphenylphosphine.

formaldehyde was an expected by-product but was not observed, apparently because of further oxidation and consumption of the resulting formate in the above reaction sequence.[2a]

A typical prodedure is given for the reduction of 2-bromonaphthalene. A mixture of 2-bromonaphthalene (0.518 g, 2.50 mmol), sodium formate (0.255 g, 3.75 mmol), 1 (0.145 g, 0.125 mmol), and DMF (5 ml) in a round-bottom flask equipped with a magnetic stirring bar was placed under nitrogen and heated at 100°C for 6 hr. The reaction mixture was cooled to 25°C and partitioned between pentane and water. From the organic layer was obtained naphthalene which was purified by sublimation to give 0.254 g (79%) of white crystals: mp 79-80°C (lit.[6] mp 80.2°C).

Further work is in progress to study the full scope of the reduction of aryl halides and other types of substrates and the use of other catalysts.

REFERENCES

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2. (a) G.M. Bogdanov and A.P. Belov, Dokl. Akad. Nauk SSSR, 232, 814 (1977); b)M.E. Vol'pin, V.P. Kukolev, V.O. Chernyshev, and I.S. Kolomnikov, Tetrahedron Lett., 4435 (1971).

3. N.A. Cortese and R.F. Heck, J. Org. Chem., 42, 3491 (1977).

4. For a brief summary of methods for reducing aryl halides see: J. March, "Advanced Organic Chemistry," 2nd ed., McGraw-Hill Book Co., New York, 1977, pp 517-518.

5. For reviews of oxidative addition see: S.D. Robinson in "Organometallic Chemistry, Vol. 5, A Specialist Periodical Report," E.W. Abel and F.G.A. Stone, Ed., The Chemical Society, London, 1976, pp 379-394, and earlier volumes in this series.

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