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ORGANIC SONOCHEMISTRY. ULTRASONIC ACCELERATION OF THE REDUCTION OF SIMPLE AND DEACTIVATED ARYL HALIDES USING LITHIUM ALUMINUM HYDRIDE

Byung Hee Han and Philip Boudjouk*

The Department of Chemistry
North Dakota State University
Fargo, ND 58105-5516

Abstract. Eleven aromatic halides are reduced in very high yields in the presence of $LiAlH_4$ and sonic waves at 35°.

Recently we have succeeded in accelerating the rates of several reactions using sonic waves.[1-3] For example, the Wurtz-type coupling of organic halides, RX, (R = alkyl, aryl, benzyl and benzoyl and X = Cl, Br and I)[1] and organometallic chlorides, R_3MCl, (R = alkyl, aryl; M = Si Sn)[2] using lithium wire at room temperature proceeds at a convenient rate only in the presence of ultrasounds. We've also found that sonication of a dioxane solution of α,α'-dibromo-o-xylene in the presence of zinc powder provides an easy route to good yields of the reactive intermediate o-xylylene[3] and that ultrasound facilitates the reaction of lithium with bis(mesityl)dichlorosilane to give good yields of tetramesityldisilene, a stable compound containing a silicon-silicon double bond.[4] These observations, in conjunction with the earlier successful rate accelerations of the Barbier reaction[5] and mercury reduction of α,α'-dibromoketones,[6] point to considerable synthetic potential for sonic waves in heterogeneous reactions. Applied to homogeneous systems, ultrasound has produced rate enhancements that are modest by comparison.[7]

That aromatic halides are reluctant substrates for nucleophilic substitution is well-known and it is generally accepted that electron-donating groups on the ring further impede displacement of the halogen. Nucleophilic hydrogen, however, in the form of complex metal hydrides, has been employed with some success in the reduction of aryl halides.[8] Bromobenzene, for example, gave a 52% yield of benzene after 6 h and 95% after 24 h when treated with a four molar excess of a tetrahydrofuran (THF) solution of $LiAlH_4$.[9] However, deactivated halides, like p-bromoanisole and p-bromotoluene, for example, produced only a 17% yield of anisole and a 20% yield of toluene, respectively under the same conditions.[9]

We have found that sonic acceleration can be applied to these systems and in this communication we report our preliminary results on the lithium aluminum hydride reductions of some simple and deactivated aryl halides. Our results are summarized in the Table.

$$\text{Ar-X} \; + \; LiAlH_4 \xrightarrow{((((} \text{Ar-H}$$

Table. Ultrasound-Accelerated Reductions of Aromatic Halides

	Ar-X	Ar-H	Yield (time,h)[a]	Comparison (yield; time; temp.; solvent)[b]
1.	o-Bromotoluene	Toluene	98% (5h)	21%; 24h; 25°, THF
2.	p-Bromotoluene	Toluene	97% (5h)	20%; 24h; 25°, THF
3.	m-Bromotoluene	Toluene	81% (6h)	
4.	o-Iodotoluene	Toluene	95% (5h)	92%; 24h; 100°; Diglyme
5.	o-Bromoanisole	Anisole	98% (4h)	58%; 24h; 100°; Diglyme
6.	p-Bromoanisole	Anisole	70% (7h)	35%; 24h; 100°; Diglyme
7.	p-Iodoanisole	Anisole	73% (7h)	91%; 24h; 100°; Diglyme
8.	1-Bromonaphthalene	Naphthalene	99% (6h)	99%; 6h; 65°; THF
9.	1-Iodonaphthalene	Naphthalene	99% (6h)	72%; 24h; 65°; THF
10.	1-Chloro-3-bromobenzene	Chlorobenzene	98% (4h)[c]	95%; 24h; 25°; THF
11.	1-Chloro-4-bromobenzene	Chlorobenzene	98% (4h)[c]	

a. All of our reactions were run at 35° in dimethoxyethane using a 1:1 molar ratio of $LiAlH_4$:ArX.

b. A 1:1 ratio of $LiAlH_4$:ArX was employed in all cases except comparison examples 8 and 10 which required ratios of 4:1 and 1.5:1 respectively.[9]

c. Traces of benzene were also observed by nmr.

Improvements in yields or reaction conditions are significant in all cases but the most dramatic differences are those observed for the deactivated halides. In a typical experiment, 10 mmol of an aromatic halide and 10 mmol of $LiAlH_4$ were added to 10 ml of dry THF. The reaction mixture, contained in a 100 ml round bottom single neck flask and maintained under a nitrogen atmosphere, was partly submerged in a common ultrasound laboratory cleaner (117 v, 150 w, 50/60 Hz). Cavitation produced a turbid reaction mixture immediately and after several hours the reaction was quenched and the products isolated.

In each case the workup procedure was the same. The product mixture was first poured slowly onto an ice-CH_2Cl_2 slurry with stirring. This was extracted twice with CH_2Cl_2 and the extracts were dried over $MgSO_4$. The solvents were removed by distillation or flash evaporation. Typically the recovery of ArX and ArH exceeded 90%. Yields were obtained by nmr analysis of the product mixture following these steps. Mole ratios of solvent:product:starting material were measured by nmr and used to compute mass balances. Our reaction conditions were not optimized and these reductions may be more efficient than indicated. The literature examples however, are optimized reactions.[9]

There are significant differences in the manner in which our reductions were carried out compared to those by Brown and Krishnamurthy.[9] Our reactions were run as heterogeneous mixtures whereas the comparison examples were THF solutions.[9] This is in concert with earlier observations that heterogeneous reactions benefit greatly from sonication.[1-5] Also, our solvent was DME which was far more effective than THF in the presence of sonic waves. The functions of surface and solvent in sonically accelerated reactions are not clearly understood and work is now in progress to elucidate the roles of these variables in the $ArX \rightarrow ArH$ transformation. Additionally, we are investigating other complex hydrides to determine if they can be activated by sound as well as broadening the scope of the $LiAlH_4$/DME reducing system to other substrates.

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