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ORGANIC SONOCHEMISTRY. ULTRASOUND-PROMOTED COUPLING OF ORGANIC HALIDES IN THE PRESENCE OF LITHIUM WIRE

Byung Hee Han and Philip Boudjouk*

The Department of Chemistry
North Dakota State University
Fargo, N.D. 58105

Abstract. Alkyl, aromatic, benzylic and benzoyl halides have been successfully coupled in good yields using lithium wire suspended in tetrahydrofuran and ultrasound.

There is a growing list of successful applications of ultrasound to organic synthesis.[1-6] Among these are the sonocleavage of halogens from aliphatic and aromatic halides,[1] the reduction of α,α'-dibromoketones by ultrasonically dispersed mercury[2] and the reductive coupling of organic bromides with ketones.[3] Very recently we discovered the facile coupling of aryl and alkylchlorosilanes using lithium and sonic waves to form disilanes.[4]

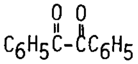
$$2R_3SiCl \xrightarrow[\text{Li,THF}]{)))} R_3SiSiR_3$$

In this paper we report that ultrasound also promotes a similar reaction with organic halides. We have examined, in this preliminary study, a broad range of organic halides, RX, that encompasses R = aryl, benzyl, benzoyl and alkyl. For R = phenyl, the chloro, bromo and iodo derivatives were surveyed. In the absence of sonic waves, little or no reaction occurs. Our results are presented in the Table.

In a typical experiment, a 50 ml flask was charged with 0.02 mol of the organic halide, an equivalent of lithium wire (1/4" x 1/8") and 5 ml of dry tetrahydrofuran. The flask was immersed to the solvent level in a common ultrasound laboratory cleaner (117v, 150w, 50/60 Hz). The product mixture was chromatographed on neutral alumina. The products were characterized by comparison of their physical and chemical properties with those of authentic samples.

TABLE

Ultrasound Induced Coupling of Organic Halides with Lithium

RX	Product	Time(hr)	Yield(%)
C_6H_5Cl	$C_6H_5\text{-}C_6H_5$	12	70
C_6H_5Br	$C_6H_5\text{-}C_6H_5$	10	70
C_6H_5I	$C_6H_5\text{-}C_6H_5$	12	73
$p\text{-}CH_3C_6H_4Br$	$(p\text{-}CH_3C_6H_4)_2$	10	52
$p\text{-}CH_3C_6H_4I$	$(p\text{-}CH_3C_6H_4)_2$	10	42
$m\text{-}CH_3C_6H_4Br$	$(m\text{-}CH_3C_6H_4)_2$	10	36
$C_6H_5CH_2Cl$	$C_6H_5CH_2CH_2C_6H_5$	40	60[a]
C_6H_5COCl	 $C_6H_5\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}C_6H_5$	17	73
$CH_3CH_2CH_2Cl$	$CH_3(CH_2)_6CH_3$	17	72

a. Yield by nmr. All others are isolated yields (>95% pure).

We are presently investigating cross-coupling reactions and organic dihalides and will report on them in due course.

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