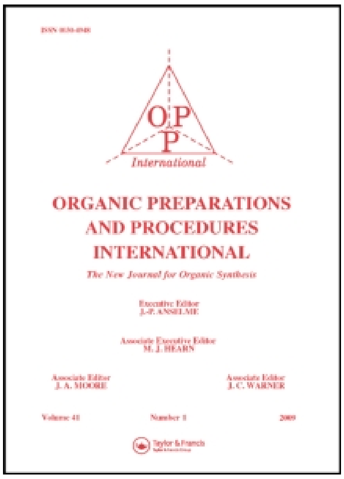

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SYNTHESIS OF ARYL HALIDES *via* ORGANOBORANE CHEMISTRY

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sulfuric acid, and 7.8% water. As used in the above table (% NSA), "60% NSA" would indicate a mixture of 60% DuPont NSA solution and 40% added water (by volume). The addition of water results in partial decomposition (with vigorous evolution of NO_x vapors) as well as dilution of the NSA. NSA concentrations and temperatures used were selected by determining the mildest conditions which would allow the hydrolysis to proceed at a convenient rate. In some cases, dichloromethane was added to the NSA solution to form a two-phase reaction mixture.

4. Structures assigned to the carboxylic acids were confirmed by comparison with authentic samples.

SYNTHESIS OF ARYL HALIDES *via* ORGANOBORANE CHEMISTRY

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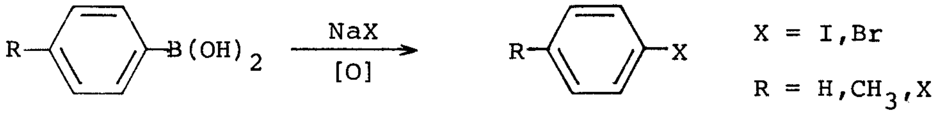
Aryl halides are generally formed *via* reaction of aryl diazonium salts with halide ions. These reactions are quite sensitive to temperature, solvent, and other factors. Nevertheless, the products are isomerically pure, in contrast to the mixtures which are obtained *via* direct halogenation of arenes. We recently developed new halogenation methods which involve the reaction of organoboranes with halide ions in the presence of chloramine-T.[1] we have found these reactions to be suitable for the rapid synthesis of a variety of functionally substituted aryl halides.



The arylboronic acids are conveniently prepared <u>via</u> reaction of aryl lithium (or Grignard) reagents with trimethyl borate and many of them are commercially available. They are easily handled solids which are stable towards hydrolysis and moderately stable towards oxidation. The reactions of arylboronic acids with halogens have been examined;[2-4] they generally require long reaction times and drastic conditions,[5] often leading to competing reactions such as oxidation[6] or addition[6,7] of the halogens to the boronic acid. The results of our study are presented in Table 1.

TABLE 1. Halogenation of Arylboronic Acids

Boronic Acid	Product[a]	Yields (%) Iodination	Yields (%) Bromination
$C_6H_5B(OH)_2$	C_6H_5-X	87	89
p-$CH_3C_6H_4B(OH)_2$	p-$CH_3C_6H_4X$	88	80
p-$BrC_6H_4B(OH)_2$	p-BrC_6H_4X	85	83
p-$HO_2CC_6H_4B(OH)_2$	p-$HO_2CC_6H_4X$	79	61

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[a] The products indicated contain iodine and bromine respectively. All products exhibited physical and spectral characteristics in accord with authentic samples.

EXPERIMENTAL

Benzeneboronic acid and p-bromophenylboronic acid were purchased from Aldrich Chemical Co. p-Tolueneboronic acid[8] and p-carboxyphenylboronic acid were prepared according to established procedures.

Halogenation. General Procedure.- The arylboronic acid (2 mmol) was dissolved in 8 ml of 50% aqueous methanol in a round bottomed flask which was shielded from light. Aqueous sodium halide (2.5 mmol, 2.5 ml of a 1.0 N solution) was added, followed by chloramine-T (4.0 mmol, 0.9 g) dissolved in 8 ml of 50% aqueous methanol. [In the bromination reactions,4 ml of 10% aqueous HCl were added at this stage.] The reaction mixture was stirred for 15 minutes at room temperature (color fades)[10] and then diluted with 20 ml of water. The product was extracted into ether, the solution dried over anhydrous $MgSO_4$, and the solvent removed. The products were purified by column chromatography on silica gel using 90:10 petroleum ether-ethyl acetate as eluent.

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10. Longer reaction times appear to be detrimental.

FACILE OXIDATIVE CLEAVAGE OF CARBON-CARBON MULTIPLE BONDS WITH CHROMIUM(V) REAGENT [(BiPy)H_2CrOCl_5]

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Recently we reported[1] the use of chromium(V) reagents for the oxidation of alcohols to carbonyl compounds and of aldehydes to carboxylic acids. We now report a facile oxidative cleavage of carbon-carbon multiple bonds in the absence of readily oxidisable alcohol or aldehyde groups. The oxidation of carbon-carbon multiple bonds with different chromium(VI) reagents is often complicated by various side-reactions.[2] In general it has been observed that in a partially aqueous medium, chromic acid favors oxidative cleavage of carbon-carbon multiple bonds whereas anhydrous conditions favor either attack at allylic positions or partial oxidation of the double bond to form epoxides, diol derivatives or ketols; rearrangement of the intermediate oxidation products has also been observed.

We have now found that the chromium(V) complex [(BiPy)H_2-$CrOCl_5$][3] effects a fairly clean oxidative cleavage of carbon-