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Simple Procedure for the Conversion of Aryl Halides to the Corresponding Phenols

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The use of two well known reactions in series has afforded a relatively rapid and efficient route from aryl halides to the corresponding phenols. The overall reaction sequence employed is illustrated in the following formulation.

$$\mathrm{ArX} \longrightarrow \mathrm{ArMgX} \xrightarrow[2.\ \mathrm{H_2O,\ H^+}]{1.\ \mathrm{B(OCH_3)_3}} \begin{matrix}\mathrm{ArB(OH)_2}\\ + \\ \mathrm{Ar_2B(OH),\ etc.}\end{matrix} \xrightarrow{10\%\ \mathrm{H_2O_2}} \mathrm{ArOH} + \mathrm{B(OH)_3}$$

The simplicity of the method lies in the fact that the arylboronic acid, which is produced along with varying amounts of other materials having aryl-boron bonds, need not be isolated. Treatment of the crude product (in ethereal solution) with 10% hydrogen peroxide readily degrades the product mixture to the corresponding phenol in 60–80% overall yield (based on aryl halide). The method has been applied to the preparation of phenol, α-naphthol and *p*-cresol which were obtained in 78, 75, and 60% yields, respectively.

EXPERIMENTAL

The experimental procedure is illustrated by the preparation of phenol. To a one-liter three-neck flask equipped with a stopcock on its bottom and carrying a reflux condenser, dropping funnel, stirrer, nitrogen inlet, and drying tube, was added 31 g. (0.33 mole) of pure methyl borate and 400 ml. of dry ether. The apparatus was flushed with dry nitrogen and 200 ml. of 1.5*M* phenylmagnesium bromide was added dropwise over a period of 1 hr. while the contents of the flask were cooled to −80° and rigorously stirred. After the addition the reaction mixture was warmed to room temperature and 200 ml. of 10% hydrochloric acid slowly run in with stirring under nitrogen. The stirrer was stopped and the lower aqueous phase separated by use of the stopcock in the flask bottom. The ether layer was washed twice more with water in this fashion. Two hundred milliliters of 10% hydrogen peroxide was slowly added from the dropping funnel with stirring at such a rate as to maintain gentle reflux. After the addition the mixture was stirred for 15 min. and the layers separated as before. The ether layer was washed with 10% ferrous ammonium sulfate and the phenol extracted by two portions of 10% sodium hydroxide solution. Acidification of the alkaline extract followed by extraction with ether and distillation afforded 22.0 g. (78% theory) of pure phenol, melting at 40–41°.

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Rauwolfia Alkaloids. V.[1] Stereochemical Correlation of Some Indole Alkaloids from the Infrared Spectra

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In a series of publications on Rauwolfia[2] alkaloids from these laboratories, we have used spectral data for deduction of structural features of reserpine,[3] reserpinine,[4] and deserpidine (recanescine).[5]

Our technique consisted of comparing the infrared spectrum of the naturally occurring alkaloid in chloroform solution[3] with the spectrum of an equimolar solution of a substituted methoxyindole and suitable component, bearing the remaining functional groups of the alkaloid. In the case of reserpinine, for example, it was pointed out that the identity of the wave lengths and intensities of most of the corresponding bands in the spectra of reserpinine and summation of 2,3-dimethyl-6-methoxyindole and tetrahydroalstonine strongly suggests the same steric configuration in these two alkaloids.[4]

After the compilation of the physical data of indole and dihydroindole alkaloids[6] we had on hand the infrared spectra of several heteroyohimbane derivatives in chloroform solution.

A close examination of these spectra permits the assignment of a methoxylated derivative to the tetrahydroserpentine or tetrahydroalstonine series.[7] The present paper deals with our observations in this class of indole alkaloids.

In our studies we have used the following indole alkaloids, derivatives of the heteroyohimbane ring system: aricine (VI),[8] reserpinine (III),[4] isoreserpiline (VIII),[8] raumitorine (VII),[9] tetra-

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[1] For paper IV of this series, see S. C. Pakrashi, Carl Djerassi, Richard Wasicky, and N. Neuss, *J. Am. Chem. Soc.*, **77**, 6687 (1955).

[2] In strict usage and in compliance with the International Code of Botanical Nomenclature, the name should be spelled Rauvolfia, J. Monachino, *Economic Botany*, **8**, 349 (1954).

[3] N. Neuss *et al.*, *J. Am. Chem. Soc.*, **76**, 2463 (1954).

[4] N. Neuss *et al.*, *J. Am. Chem. Soc.*, **76**, 3234 (1954) and references cited therein.

[5] N. Neuss *et al.*, *J. Am. Chem. Soc.*, **77**, 4087 (1955).

[6] Lilly collection of Physical Data of Indole and Dihydroindole Alkaloids, Lilly Research Laboratories, Eli Lilly and Co., Indianapolis 6, Ind., 1954 and 1956.

[7] E. Wenkert and D. K. Roychaudhuri, *J. Am. Chem. Soc.*, **78**, 6417 (1956), have just classified different indole alkaloids into normal and allo compounds and pseudo or epiallo compounds on the basis of presence or absence of certain bands in the 3.4–3.7 μ region. We would like to thank Dr. Wenkert for sending us the paper prior to its publication.

[8] A. Stoll, A. Hofmann, and R. Brunner, *Helv. Chim. Acta*, **38**, 270 (1955).

[9] Janot, Goutarel, Le Hir, and Poisson, *Compt. rend.*, **239**, 302 (1954).