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TITLE

I. Ortho-Arsenated Phenoxyalkanols

II. Meta-Arsenated Phenoxyethanols

BY

Stephen Bennett Binkley

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ORTHO-ARSENATED PHENOXYALKANOLS

and

META-ARSENATED PHENOXYETHANOLS

by

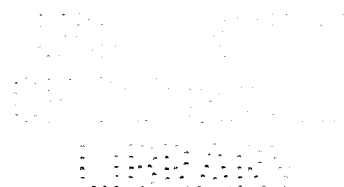
Stephen Bennett Binkley

A THESIS

Presented to the Faculty of
The Graduate College in the University of Nebraska
in Partial Fulfillment of Requirements for the
Degree of Doctor of Philosophy
Department of Chemistry

Lincoln, Nebraska

January, 1938



UMI Number: DP14041

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ACKNOWLEDGMENT

The writer wishes to express his sincere appreciation to Dr. C. S. Hamilton, who suggested the problem and supervised the work, and to Parke, Davis and Company for a research grant.

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PART I

ORTHO-ARSENATED PHENOXYALKANOLS

INTRODUCTION

Although a number of arsenated ethers of benzene have been prepared with the ether linkage in the para position, very little work has been done with arsonic acids having the ether linkage in the ortho position. In 1935 Harrington¹ prepared β -2-arsonophenoxyethanol by condensing o-hydroxyphenylarsonic acid with ethylene chlorohydrin and also by the Bart² reaction on β -2-aminophenoxyethanol, but by both procedures the yields were so low that the therapeutic value of the derivatives of this compound could not be determined. Since β -2-amino-4-arsonophenoxyethanol³ and α -methyl, β -2-amino-4-arsonophenoxyethanol⁴ showed considerable trypanocidal value it was desirable to study isomeric compounds. This part of the investigation deals with the preparation of α -methyl, β -2-arsonophenoxyethanol and its derivatives.

DISCUSSION

A large number of attempts were made to prepare α methyl, β -2-arsonophenoxyethanol by condensing o-hydroxyphenylarsonic acid with propylene chlorohydrin. Before these reactions could be attempted it was necessary to devise a convenient method for the preparation of o-hydroxyphenylarsonic acid. The Bart² reaction on o-aminophenol gave low yields and the isolation of the product was difficult. o-Nitrophenylarsonic acid was prepared in 80% yields by means of the Bart² reaction on o-aminonitrobenzene. o-Nitrophenylarsonic acid was reduced catalytically⁵ to o-aminophenylarsonic acid and was then diazotized at 0°. On warming the diazonium solution to 60° for an hour, o-hydroxyphenylarsonic acid was produced and separated in almost pure form on cooling.

Only starting material was obtained when o-hydroxyphenylarsonic acid was refluxed in 6 N sodium hydroxide with propylene chlorohydrin. No condensation was observed when an alcoholic potassium hydroxide solution was used as the condensing medium. The potassium chloride which separated during the reaction, came from the reaction of potassium hydroxide with the propylene chlorohydrin. An attempt was made to condense the dry potassium salt of o-hydroxyphenylarsonic acid with propylene chlorohydrin using absolute alcohol as a solvent but no condensation product could be isolated.

The condensation of o-nitrophenol with propylene chlorohydrin in 2 N sodium hydroxide solution gave 35% yields.