

Faculty Research Edition

of

The Savannah State College Bulletin

Published by

THE SAVANNAH STATE COLLEGE

Volume 17, No. 2 Savannah, Georgia December, 1963

WILLIAM K. PAYNE, President

EDITORIAL COMMITTEE

Blanton E. Black

Joan L. Gordon

Charles Pratt

J. Randolph Fisher

E. J. Josey

Forrest O. Wiggins

John L. Wilson, Chairman

Articles are presented on the authority of their writers, and neither the Editorial Committee nor Savannah State College assumes responsibility for the views expressed by contributors.

Contributors

Arthur L. Brentson, Assistant Professor of English

T. T. Chao, Professor of Chemistry, Fayetteville State Teachers College,
North Carolina

James A. Eaton, Professor of Education

Dorothy C. Hamilton, Assistant Professor of Education

Phillip J. Hampton, Assistant Professor of Fine Arts

Thelma Moore Harmond, Associate Professor of Education

Elonnie J. Josey, Librarian and Associate Professor

Walter A. Mercer, Professor of Education and Director of Internship
Teaching, Florida A.&M. University, Tallahassee, Florida

Luetta C. Milledge, Assistant Professor of English

Malvin E. Moore, Professor of Education, and Dean, Fayetteville State
Teachers College, North Carolina

Louise Lautier Owens, Associate Professor of English

Evanel Renfrow Terrell, Associate Professor of Home Economics

Willie G. Tucker, Associate Professor of Chemistry

Nazir A. Warsi, Associate Professor of Mathematics

W. Virgil Winters, Professor of Mathematics and Physics

The Savannah State College Bulletin is published October, December, February, March, April, and May by Savannah State College. Entered as second-class matter, December 16, 1947, at the Post Office at Savannah, Georgia under the Act of August 24, 1912.

TABLE OF CONTENTS

	Page
How Practices and Attitudes Regarding Marking and Reporting in a Sampling of Randomly Selected Secondary Schools Compare with Research Findings in the Area	5
Thelma Moore Harmond	
The Chlorination of Pyridine with Cupric Chloride	17
Willie G. Tucker	
On Curved Shock Waves in 3-Dimensional Unsteady Flow of Conducting Gases	20
Nazir A. Warsi	
Using Class Projects As Indexes of Student's Feelings	32
James A. Eaton	
Some Practices in Conducting Programs of Off-Campus Student Teaching in Selected Institutions of Georgia	37
Walter A. Mercer	
A Correlation Study on Grades Between High Schools and Fayetteville State Teachers College	42
T. T. Chao and Malvin E. Moore	
Honey in the Carcass: A Study of Some Antipodal Imagery in <i>All The King's Men</i>	50
Luetta C. Milledge	
A Review of Pertinent Literature on the Nutritional Status of the Negro Child: 1919-1954	55
Evanell Renfrow Terrell	
Enhancing and Strengthening Faculty-Library Relationships	65
Elonnie J. Josey	
Whitman's Attitude Toward Humanity, Death, and Immortality	73
Arthur L. Brentson	
Superconducting Magnets	91
W. Virgil Winters	
The Life and Works of Johann Heinrich Pestalozzi	94
Dorothy C. Hamilton	
An Approach to Art for Preadults	106
Phillip J. Hampton	
Language in Government—and Elsewhere	112
Louise Lautier Owens	

The Chlorination of Pyridine With Cupric Chloride

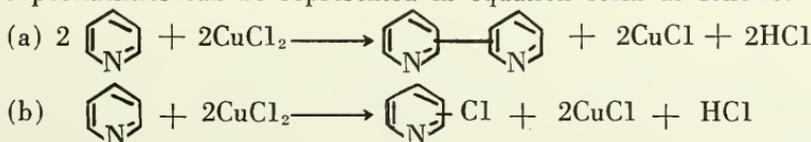
by

Willie G. Tucker

The purpose of this investigation was to study the liquid phase reaction of cupric chloride and pyridine or pyridine salts, as a method of introducing halogen into the pyridine ring.

The usual methods for introducing halogen into homocyclic aromatic ring compounds, such as benzene, are not practical for pyridine. Benzene can be chlorinated or brominated with the free halogen in good yields at moderate temperatures, whereas pyridine can be directly chlorinated and brominated only in the vapor phase at temperatures from 250°C to 450°C. The replacement of the primary amino group with halogen through a diazonium salt intermediate is generally applicable to homocyclic aromatic ring compounds. The requisite primary amines are easily prepared by reduction of the nitro-aromatic compounds, which are in turn, easily prepared by direct nitration of the hydrocarbon. By contrast, direct nitration of the pyridine ring requires extremely drastic conditions; amino groups on the 2- and 4- positions of the pyridine ring do not give the normal diazonium reaction. These circumstances have necessitated the use of special methods, which are described below for the introduction of halogen into the pyridine ring.

The idea of the use of cupric chloride as a chlorinating agent grew out of the observation that in the Ladenburg rearrangement (1) of alkyl-pyridinium halides to 2- and 4- alkyl pyridines, cupric chloride could be substituted for the presumed catalyst, cuprous chloride. If it is assumed that in this reaction the cupric chloride is reduced to cuprous chloride, it must follow the cupric chloride is oxidizing something. The two most likely suppositions are [a] the formation of bipyridyle and [b] the halogenation of the pyridine ring. These two possibilities can be represented in equation form as follows:



EXPERIMENTAL

This experimental work was begun with no clear idea as to how to start because similar reactions from which procedures could be imitated or modified, were not found in the literature. Lacking such precedents, a series of procedures were tried in the hope that some combination of conditions would be found which would give some yield of a recognizable product. After finding such favorable conditions, if they could be found, it was hoped and assumed that further experimentation could be carried out in a more logical sequence.

The first phase of this work turned out to be long, discouraging, and unproductive. Little, if any, information was obtained from which inferences could be made and upon which the next experiments could be planned. From hindsight there was a two-fold problem [a] to find conditions under which a reasonable yield of a recognizable product was produced and [b] to find a method of isolating a product when it was produced. Both had to be resolved simultaneously.

It has been found (2) that substantial yields of 2-chloropyridine can be obtained by heating a mixture of pyridine hydrochloride and cupric chloride. No bipyridyle have been detected in the product of the reaction. Still better yields of 2-chloropyridine were obtained by introducing a slow stream of gaseous chlorine into the liquid-phase mixture of pyridine hydrochloride and copper halide salts.

It was interesting to carry out the reaction with other cupric salts to investigate the generality of the reaction; therefore, cupric bromide was also used. The yield of 2-bromopyridine, however, was poor.

In attempting to understand the reaction, it was assumed that an oxidation-reduction process was involved and the cupric salt was reduced to the cuprous salt. This led to the suggestion that the higher chloride of any element containing two valences would give some chlorination to a greater or lesser extent. The suggestion proved worthless though, as stannic chloride, phosphorus pentachloride, and ferric chloride failed to give chlorinated pyridines to any appreciable extent. Antimony pentachloride produced a 28 per cent yield of 2-chloropyridine.

Judging from Wibaut's work (3) and our research, it seems that we had to operate in a temperature range of 260°C—270°C in order to get an appreciable rate of chlorination. This temperature range could be maintained by two methods; first, the use of pressure; and secondly, the use of pyridine hydrochloride with enough cupric chloride to raise the boiling point of the hydrochloride and thus keep it in the reaction flask at the chlorination temperature. Of the two methods, operating at atmospheric pressure using pyridine hydrochloride was more convenient and of course, preferable.

To make the reaction more practical, we decided to try to regenerate the cupric chloride by passing chlorine through the residue in the reaction flask and thus make a continuous process by adding more pyridine hydrochloride and repeating the operation over and over. The process was practical and each successive run produced yields of 60 per cent or better.

A trace of bipyridyle was expected since Hein and Retter (4) reported the preparation of bipyridyle with pyridine and cupric chloride or ferric chloride at 500°C and 50 atmospheres of pressure. Since bipyridyle were not isolated or detected, it was assumed that the conditions of our reaction were not drastic enough to bring about the bipyridyle reaction even in trace amounts.

2-chloropyridine was identified by converting it into 2-methoxy pyridine and comparing the melting point of the picrate of the latter

compound with the melting point reported in the literature and with the melting point of the picrate of 2-methoxypyridine made from an authentic sample of 2-chloropyridine. Attempts to make the picrate of 2-chloropyridine were not successful.

Summary and Conclusions

Thus a convenient laboratory method, using simple equipment and inexpensive starting materials, has been developed for the preparation of 2-chloropyridine in a liquid-phase reaction, at atmospheric pressure. Consistent yields of approximately 65 per cent of 2-chloropyridine, based on the amount of pyridine consumed, can be obtained. Approximately one mole of cupric chloride must be used for each mole of pyridine initially; the residue of copper salts can be used without replenishment or purification to convert additional molar portions of pyridine to 2-chloropyridine indefinitely and without perceptible decrease in yields. This procedure could be readily adapted to continuous, rather than batch, operation if that were desired.

REFERENCES

1. Crook, K. E., *Journal American Chemical Society*, 70 (1948), 416.
2. Tucker, W. G., *A Preparation of 2-chloropyridine*, Unpublished Ph.D., dissertation, University of Oklahoma, (1962), 34 pp.
3. Wibaut, J. P., *Recueil des Travaux Chimiques des Pays-Bas*, 58 (1939), 709.
4. Hein, F., and Retter W., *Berichte*, 61 (1928), 1790.