

**A COMPARATIVE STUDY OF THE
REACTIONS OF NITROSOPHENOL
AND N-CHLOROQUINONIMINE
WITH AROMATIC AMINES**

Published @ 2017 Trieste Publishing Pty Ltd

ISBN 9780649164523

A comparative study of the reactions of nitrosophenol and n-chloroquinonimine with aromatic amines by Carleton Edgar Curran

Except for use in any review, the reproduction or utilisation of this work in whole or in part in any form by any electronic, mechanical or other means, now known or hereafter invented, including xerography, photocopying and recording, or in any information storage or retrieval system, is forbidden without the permission of the publisher, Trieste Publishing Pty Ltd, PO Box 1576 Collingwood, Victoria 3066 Australia.

All rights reserved.

Edited by Trieste Publishing Pty Ltd.
Cover @ 2017

This book is sold subject to the condition that it shall not, by way of trade or otherwise, be lent, re-sold, hired out, or otherwise circulated without the publisher's prior consent in any form or binding or cover other than that in which it is published and without a similar condition including this condition being imposed on the subsequent purchaser.

www.triestepublishing.com

CARLETON EDGAR CURRAN

**A COMPARATIVE STUDY OF THE
REACTIONS OF NITROSOPHENOL
AND N-CHLOROQUINONIMINE
WITH AROMATIC AMINES**

**A Comparative Study of the Reactions of
Nitrosophenol and *N*-Chloroquinonimine
with Aromatic Amines**

DISSERTATION

**PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIRE-
MENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE GRADUATE SCHOOL OF THE OHIO
STATE UNIVERSITY**

BY

CARLETON EDGAR CURRAN

Dupont Fellow, 1918-19, 1919-20

**THE OHIO STATE UNIVERSITY
1921**

100

UNIV. OF
CALIFORNIA

THE UNIVERSITY OF CALIFORNIA LIBRARY
400 TOWN HALL
DURHAM, N. C. 27706

UNIVERSITY OF CALIFORNIA LIBRARY
400 TOWN HALL
DURHAM, N. C. 27706

UNIVERSITY OF CALIFORNIA LIBRARY
400 TOWN HALL
DURHAM, N. C. 27706

UNIVERSITY OF CALIFORNIA LIBRARY
400 TOWN HALL
DURHAM, N. C. 27706

TABLE OF CONTENTS

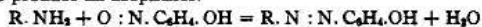
	Page
Introduction	5
Constitution of the mineral acid salts of phenylazophenol	6
Reaction of nitrosophenol with aromatic amines	8
Reaction of <i>N</i> -chloroquinonimine with aromatic amines	11
Discussion of experimental results, and conclusions:	
1. Mechanism of the nitrosophenol-aniline condensation	12
2. Theory of indophenol formation	15
3. Reactions of <i>N</i> -chloroquinonimine with aromatic amines	16
Experimental Part:	
Preparation of nitrosophenol	18
Preparation of the sodium salt of nitrosophenol	19
Preparation of <i>N</i> -chloroquinonimine	19
Preparation of phenylazophenol hydrochloride	20
Condensation of nitrosophenol with aniline and <i>p</i> -toluidine	20
Reaction of <i>N</i> -chloroquinonimine with aniline and <i>p</i> -toluidine	27
Reaction of aniline with phenylazophenol hydrochloride	30
Summary	30
Acknowledgment	31
Autobiography	32

INTRODUCTION

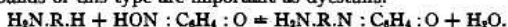
Nitrosophenol may be caused to react with primary aromatic amine without difficulty. The variety and character of the condensation products, however, do not serve to indicate clearly the manner in which the reaction proceeds. Indeed, consideration of the facts from varying stand-points might lead to opposite interpretations.

The tautomerism displayed by nitrosophenol, which under varying conditions may function either as a true phenol or as quinone oxime, suggests at least three very interesting possible reactions:

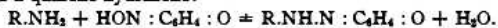
(1) Nitrosophenol, acting as a true phenol, may condense with the amine to produce an azophenol:



(2) With nitrosophenol functioning as an oxime condensation might conceivably result in the combination of a hydrogen atom from the amine nucleus with the hydroxyl of the oxime group, forming an indophenol. Compounds of this type are important as dyestuffs.



(3) Or again, condensation might be effected in such a manner as to produce a quinone hydrazone:



Experimental evidence may be adduced to support each of these possible reactions.

It has long been known that certain tertiary aromatic amines will react in accordance with reaction (2), indophenols or indamines being formed. A similar reaction is said to be employed by commercial dye manufacturers wherein primary amines and nitroso compounds are used as raw materials. However, reviewing the literature of previous investigations discloses very little information relative to such reactions. The object of this work has been, therefore, to study the condensation taking place between nitrosophenol and the aromatic amines, especially aniline and *p*-toluidine, in order to discover the mechanism of the reaction.

Three lines of experimental work were found necessary in the course of the investigation, as follows:

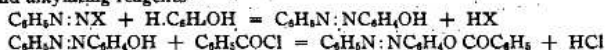
1. A study of the mineral acid salts of phenylazophenol (hydroxyazobenzene), and their reaction with aniline.
2. A study of the course of the reaction between nitrosophenol and the aromatic amines, with the isolation and identification of the various reaction products.
3. A comparative study of the reaction between *N*-chloroquinonimine (quinonechlorimide) and the aromatic amines, because of the similarity of constitution of the former to that of nitrosophenol.

In the following a brief outline of the historical development of each of these fields is given. A statement of the results of the experimental work follows, together with conclusions to be drawn therefrom. A report of the actual experimental methods and data completes the paper.

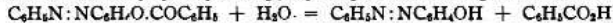
I

THE CONSTITUTION OF THE SALTS OF PHENYLAZOPHENOL

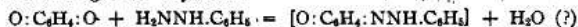
The commonly accepted configuration for phenylazophenol follows from its synthesis by the reaction of diazonium salts with phenol in alkaline solution¹ and the ready formation of its esters with the various acylating and alkylating reagents:²



This ester is readily hydrolyzed to phenylazophenol according to the reaction:



However, investigations of the acylated hydrazones of quinone have had a considerable part in determining the true nature of phenylazophenol. Zincke³ pointed out that free phenylhydrazine, or its salts, reacts with quinone with decomposition and evolution of gases, although the following reaction might be expected:



When certain substituted hydrazines, *i. e.*, the unsymmetrical acyl derivatives, are used normal reaction products are obtained:

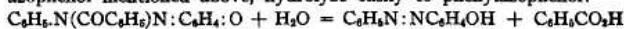


¹Griess, *Ann.* 137, 84 (1866); Kekule and Hildegh, *Ber.* 3, 234 (1870); Dimroth, *ibid.* 35, 2862.

²Tschirwinsky, *Ber.* 6, 561 (1873); McPherson, *Am. Chem. J.* 22, 364 (1899).

³Zincke, *Ber.* 16, 1563 (1883).

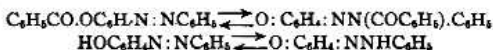
These compounds, which are isomeric with the true esters of phenylazophenol mentioned above, hydrolyze easily to phenylazophenol:



The relationship existing between these unsymmetrical acylphenylhydrazones and the true esters of phenylazophenol was largely cleared up by the work of McPherson and others¹ by synthesis and comparison of the two isomeric forms. Willstätter and Veraguth² accomplished the direct conversion of one form to the other by the action of powdered potassium hydroxide upon quinone α -benzoylphenylhydrazone in absolute ether:

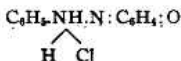


The results of these investigations proved that the acyl ester of phenylazophenol and quinone α -acylphenylhydrazone are tautomers. Similar reasoning may be applicable in explaining the true nature of phenylazophenol. That is, phenylazophenol is tautomeric with quinone phenylhydrazone. The relationship may be best shown by the following formulas:



This tautomeric explanation is especially interesting in the light of investigations of the action of concentrated mineral acids upon phenylazophenol.

Hantzsch³ has prepared and isolated the hydrochloride of phenylazophenol and has assigned to it the configuration of a quinone phenylhydrazone:



It has been noticed by McPherson and Dubois⁴ that a similar salt is formed either by the action of sulfuric acid upon phenylazophenol or of α -benzoylhydrazine sulfate with quinone:

¹McPherson, *Am. Chem. J.* 22, 364 (1899); McPherson and Gore, *ibid.* 25, 485 (1901); McPherson and Dubois, *J. Am. Chem. Soc.* 30, 816 (1908); McPherson and Fischer, *ibid.* 22, 141 (1900).

²Willstätter and Veraguth, *Ber.* 40, 1432 (1907).

³Hantzsch, *ibid.* 32, 3091 (1899).

⁴McPherson and Dubois, *J. Am. Chem. Soc.* 30, 816 (1908).