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PREVIEW

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ELECTROCHEMICAL STUDIES OF ORGANOIODINE COMPOUNDS

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PREVIEW

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ELECTROCHEMICAL STUDIES OF ORGANOIODINE COMPOUNDS

by

Shu-Chiung Wang Chen

A DISSERTATION

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

Major: Chemistry

Under the Supervision of Professor Henry E. Baumgarten

Lincoln, Nebraska

July, 1982

TITLE

ELECTROCHEMICAL STUDIES OF ORGANOIODINE COMPOUNDS

BY

Shu-Chiung Wang Chen

APPROVED

DATE

<u>Professor Henry E. Baumgarten</u>	<u>June 15, 1982</u>
<u>Professor Robert C. Larson</u>	<u>June 15, 1982</u>
<u>Professor James H. Locker</u>	<u>June 15, 1982</u>
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PREVIEW

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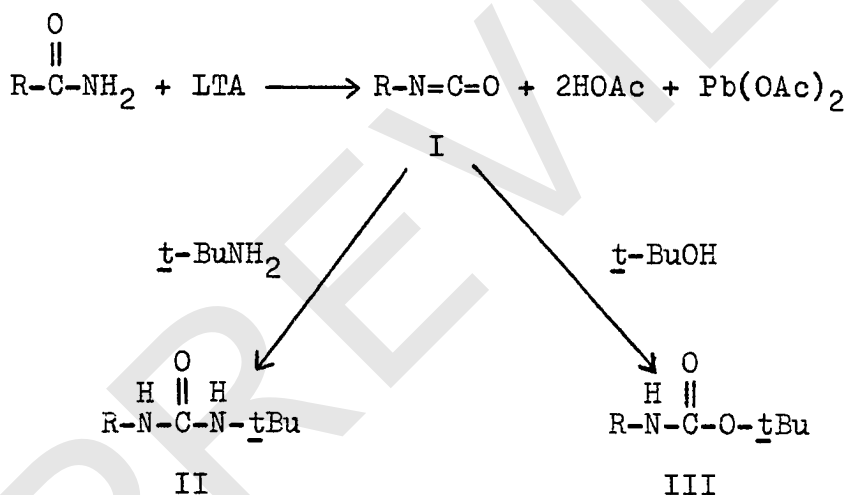
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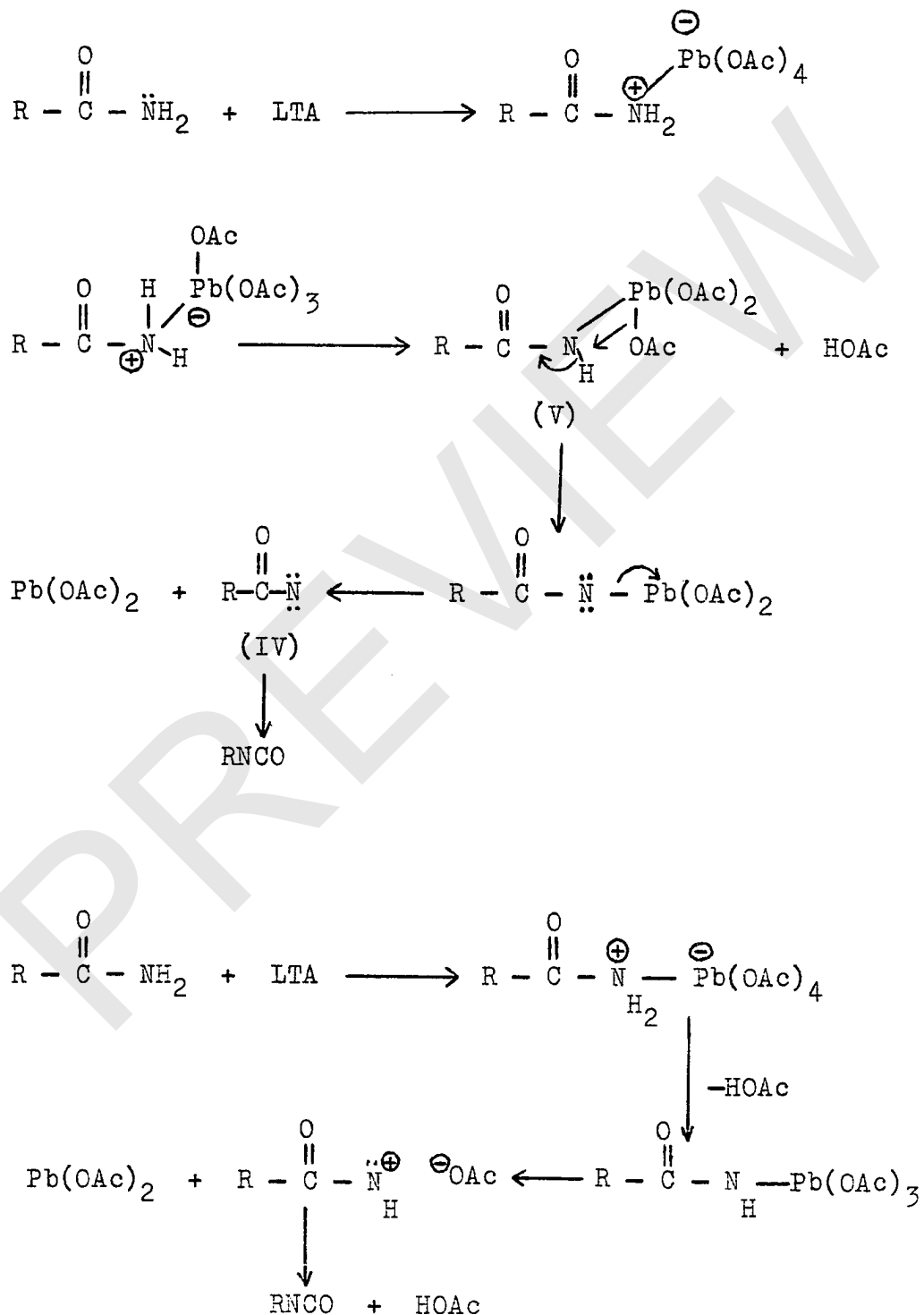
INTRODUCTION

Lead tetraacetate (abbreviated as LTA) has been widely used as an oxidizing agent in organic chemistry for a long time. The oxidation of primary amides with LTA was first reported in 1965 by Baumgarten and Staklis.¹ Various amides were found to rearrange to the isocyanate when treated with LTA in t-butyl alcohol or N,N-dimethyl formamide. The isocyanate (I) was isolated in one case, and derivatives of the isocyanates, t-butylureas (II) and t-butyl carbamates (III) were also isolated.

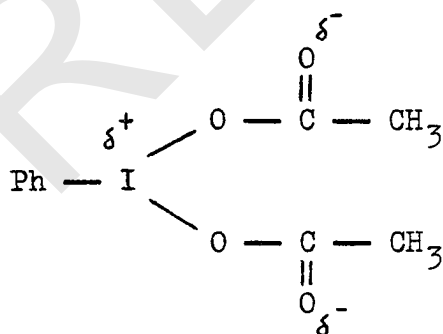


The suggested mechanism involves initial attack of the amide nitrogen on LTA to form a lead-nitrogen bond, followed by loss of acetic acid intramolecularly resulting in the formation of a nitrene (IV),¹ or nitrenium ion,² which rearranges to the isocyanate. The initial attack could take place equally easily at the amide oxygen, a process not easily distinguished from attack on nitrogen

as the lead is probably bonded to both nitrogen and oxygen in the intermediate (V)³ (vide infra).

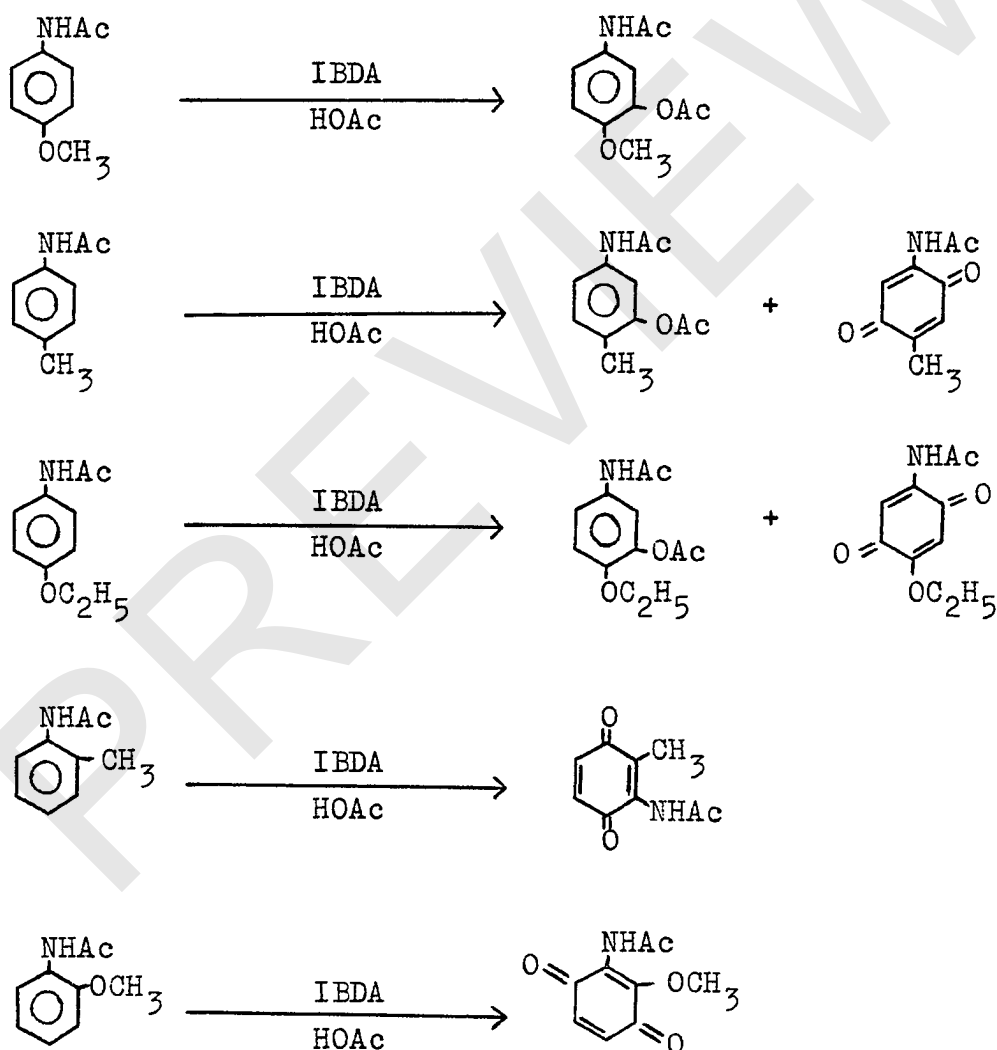


Iodosobenzene diacetate (also known as phenyliodosoacetate and diacetoxyiodobenzene) was first prepared by Willgerodt in 1892.⁴ The reagent has often been compared with lead tetraacetate, but in general has received less attention. There are many similarities between iodosobenzene diacetate and lead tetraacetate as oxidants.⁵ Iodosobenzene diacetate as an oxidizing agent brings about both free radical and ionic reactions,⁶ although iodosobenzene diacetate appears not to ionize in solution.⁷ (Conductance studies of iodosobenzene diacetate in acetic acid show a small degree of ionic dissociation above room temperature.⁶) Bell and Morgan⁸ observed that the carbonyl frequency of the ester moiety of iodosobenzene diacetate is approximately 100 cm^{-1} less than normal for ester; therefore, a Zwitterion structure was proposed:

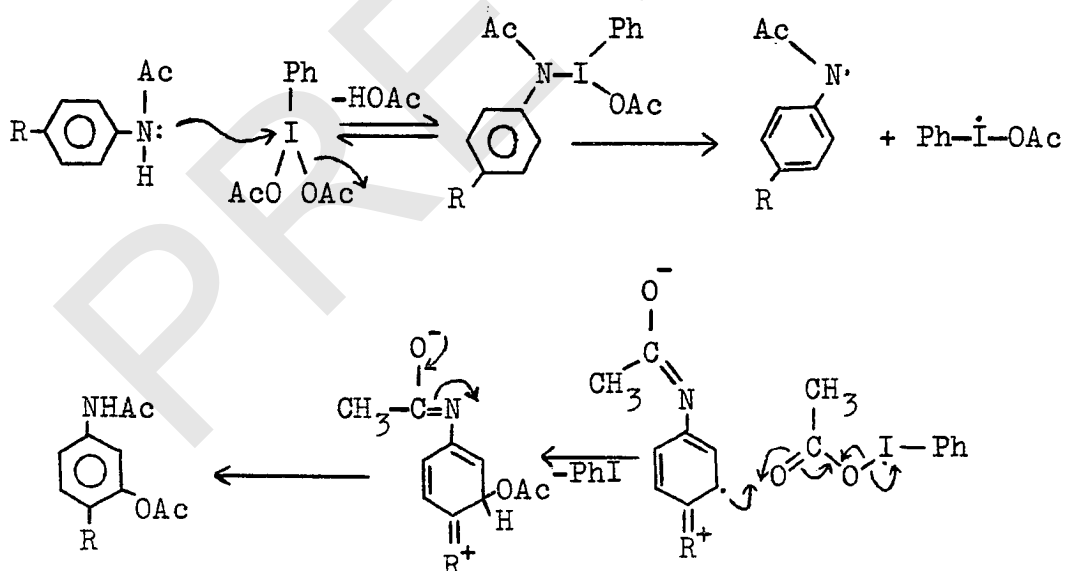


The reaction of iodosobenzene diacetate with substituted acetanilides was first studied by Barlin and Riggs.⁹ In glacial acetic acid electron-releasing substituents in the para-position gave good yields (60-70%) of the m-acetoxy acetanilides and small amounts of

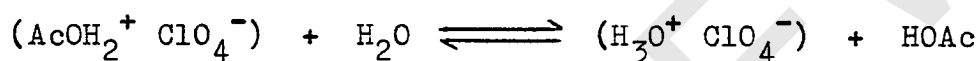
70%) of the m-acetoxy acetanilides and small amounts of quinone. With electron-releasing groups in the meta-position there was no reaction. Substitution in the ortho-position led to the formation of quinoid products. Unsubstituted acetanilide, N-methylaceto-p-toluidide, and chloro- or nitro-acetanilides did not react.



Barlin and Riggs suggested that the acetoxylation proceeds via an ionic mechanism and that the reaction is an electrophilic substitution ortho to an electron-releasing group. Later Johnson and Riggs¹⁰ investigated the kinetics of acetoxylation and found it to be a second order reaction, i.e. first order with respect to both the oxidant and the N-arylacetamide. A free radical mechanism was proposed as there is evidence that other reactions of iodosobenzene diacetate may involve free radicals.^{11,12,13,14} The acetoxylation was said to involve the initial fast and reversible formation of an intermediate by reaction at the amino group, followed by the fission of the iodine-nitrogen bond with the formation of the free radical, which undergoes the actual nuclear acetoxylation.



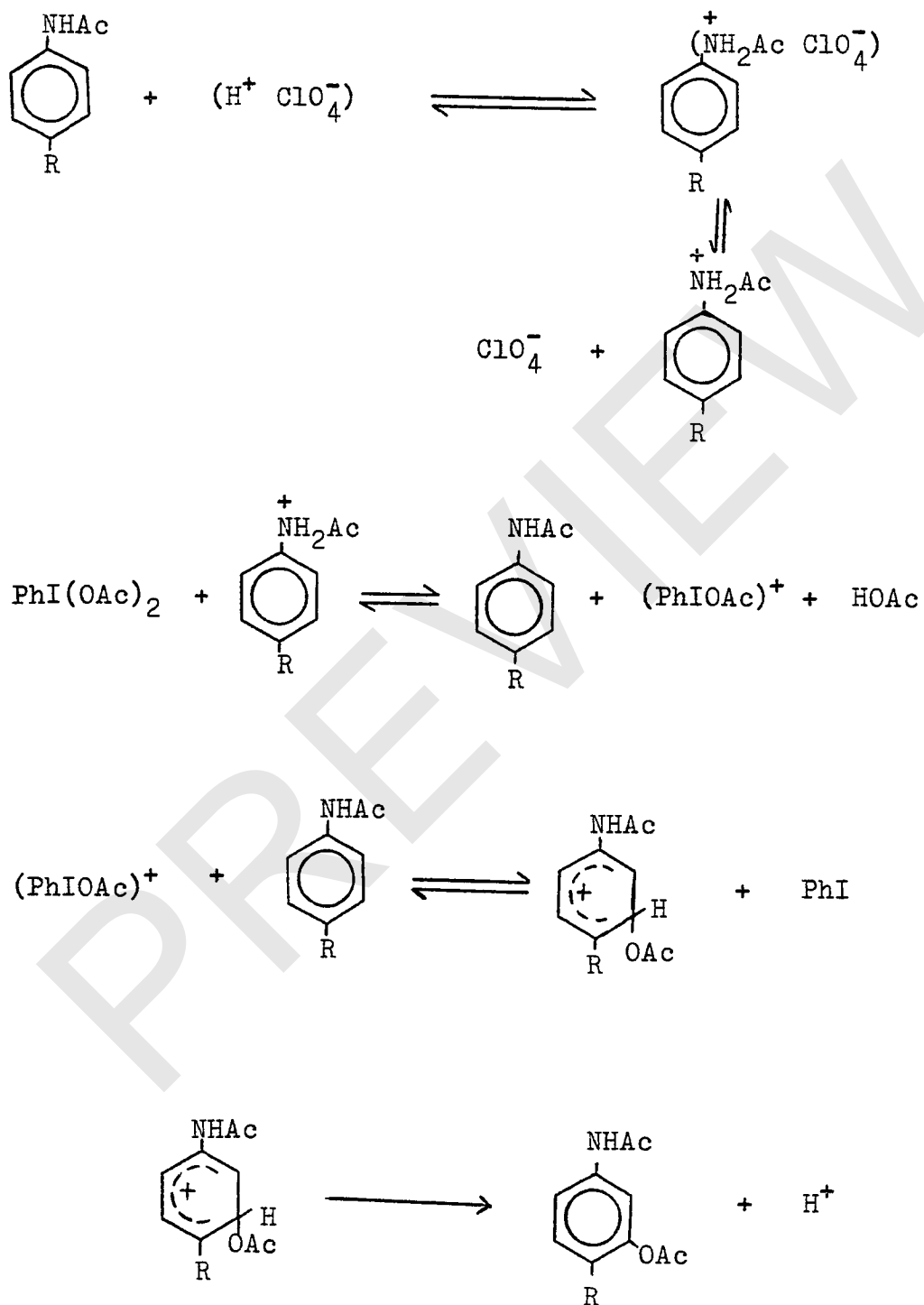
Johnson and Sherwood found that the addition of sodium acetate or sodium perchlorate had little effect on the rate of reaction but that the addition of perchloric and sulfuric acids greatly accelerated the rate. Acetic anhydride increased the reactivity slightly, but under acid conditions a small amount of water drastically reduced the rate, possibly because water becomes a weak base.^{15,16}



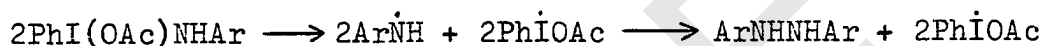
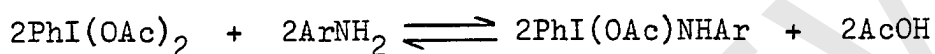
There is considerable evidence for the existence of the phenylacetoxonium ion. Johnson and Sherwood showed that iodosobenzene diacetate interacted with perchloric acid in acetic acid solutions. Hydrogen ion appeared to catalyse the dissociation.¹⁷



Based on their kinetic studies Johnson and Sherwood proposed an ionic mechanism for the acetoxylation in acid media with hydrogen ions acting catalytically.¹⁵ An electrophilic mechanism has also been proposed for acetoxylation by lead tetraacetate.^{18,19}



From the oxidation of various anilines with iodoso-benzene diacetate in benzene Pausacker¹² obtained the corresponding azo compounds in yields ranging from 3% for o-anisidine and α-naphthylamine to 95% for the conversion of aniline to azobenzene. A free radical mechanism was proposed:



Any substituent which is capable of stabilizing the radical cation would favor the formation of the azo compound.¹³ The oxidation of anilines in acetic acid gave results different from those reported above.²⁰ No azo compound was isolated if the oxidation was carried out in acetic acid, although most anilines gave good yields of the corresponding azo compounds in benzene. The oxidation of 2-naphthylamine gave 1,2,6,7-dibenzophenazine or 2-acet-amido-1,4-naphthaquinone in benzene or acetic acid, respectively.