

REACTIONS OF VARIOUS AROMATIC NITRO-COMPOUNDS  
AND ANTHRAQUINONES  
WITH SELECTED BASES AND NUCLEOPHILES

MAGDY LABIB KALDAS,  
B.Sc.  
Department of Chemistry

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### ABSTRACT

The Introduction deals mainly with historical studies on aryne chemistry and ring closure via arynes, hydride replacement from aromatic rings by nucleophiles, cleavage of anthraquinones in basic medium and the Leuckart reaction.

This work can be divided into two main sections. Section I is concerned with the investigation of the reaction of some aromatic nitro-compounds with potassamide in liquid ammonia. 3-Amino-4-nitrobenzophenone was obtained from the reaction of 4-nitrobenzophenone with this reagent, together with benzoic acid formed in a competing Haller-Bauer reaction.

Nitrobenzene under these conditions gave a complex mixture from which 2-phenylphenol was isolated; a reaction involving benzyne may be involved.

4-Nitrodiphenyl sulfone gave 4-aminodiphenyl sulfone and 4-nitroaniline. 4-Ethoxydiphenyl sulfone and 4-ethoxynitrobenzene were isolated when ethanol was used as a co-solvent in the reaction.

Oxidative coupling reactions were observed with nitrotoluenes. 4-Nitrotoluene gave 4,4'-dinitrobibenzyl which in a prolonged reaction gave 4,4'-dinitrostilbene. 2-Nitrotoluene gave 2,2'-dinitrobibenzyl, but not the corresponding stilbene derivative even after a longer time. A rather interesting result was obtained with 1-nitro-2,4,6-trimethylbenzene which gave a stilbene derivative only. Also the corresponding stilbene was obtained from bis-(4-nitrophenyl)-methane in a rather slow reaction with this reagent.

Section II deals with (i) the preparation of 5-chloro-1-N-methylaminoanthraquinone and a new synthesis of N-methylacridones and (ii) treatment of chloro-anthraquinones with formamide and a new synthesis of chloro-anthracenes.

5-Chloro-1-N-methylaminoanthraquinone was synthesised from 1,5-dichloroanthraquinone by treatment with N-methylformamide. Treatment of 5-chloro-1-N-methylaminoanthraquinone with potassamide in liquid ammonia or with potassium t-butoxide in t-butylbenzene gave N-methylacridone-1-carboxylic acid. This pleasing result, the outcome of ring opening and alternative ring closure, is being extended to related ring systems.

### ACKNOWLEDGEMENTS

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To my parents

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# I N T R O D U C T I O N

The research described in this thesis is divided into two main parts. The first is concerned with the behaviour of various aromatic nitro-compounds when treated with potassamide in liquid ammonia, and the second with treatment of selected anthraquinones and related compounds with formamide and N-methylformamide, first undertaken to provide intermediates for a new synthesis and later extended. Aspects of aryne chemistry, nucleophilic substitution, and the Leuckart reaction which relate to this work are discussed in the introduction.

### Section I

#### TREATMENT OF AROMATIC NITRO-COMPOUNDS WITH POTASSAMIDE IN LIQUID AMMONIA

##### Introductory comment.

Treatment of aromatic nitro-compounds with potassamide might involve deprotonation or nucleophilic substitution. Such steps in related systems are considered first. Aromatic nitro-compounds are well known as very reactive compounds to undergo nucleophilic substitution upon their treatment with nucleophiles. Nitro-group, as well as an effective group for stabilizing a negative charge should inductively be able to make the ortho hydrogens to it acidic enough to <sup>be</sup> removed by strong base such as potassamide in liquid ammonia. However, we found this an interesting subject to investigate.

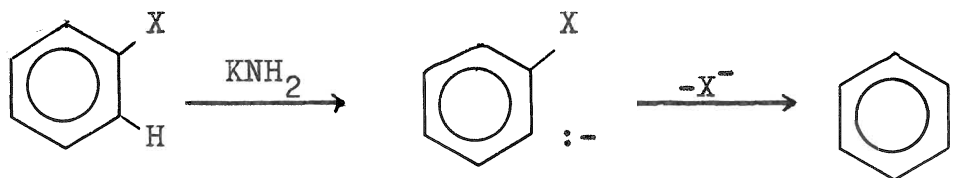
(I) The formation of aryne (Benzyne) from ortho-anionized benzene derivatives.

Several reviews have appeared on the subject of benzyne chemistry. A good introduction to the subject is provided in a review by Bunnett<sup>1</sup>. More recently a comprehensive monograph<sup>2</sup> has appeared on the subject.

Today a variety of paths to benzyne intermediate are known. One of the easiest routes to benzyne intermediate involves the metallation of aryl halides.

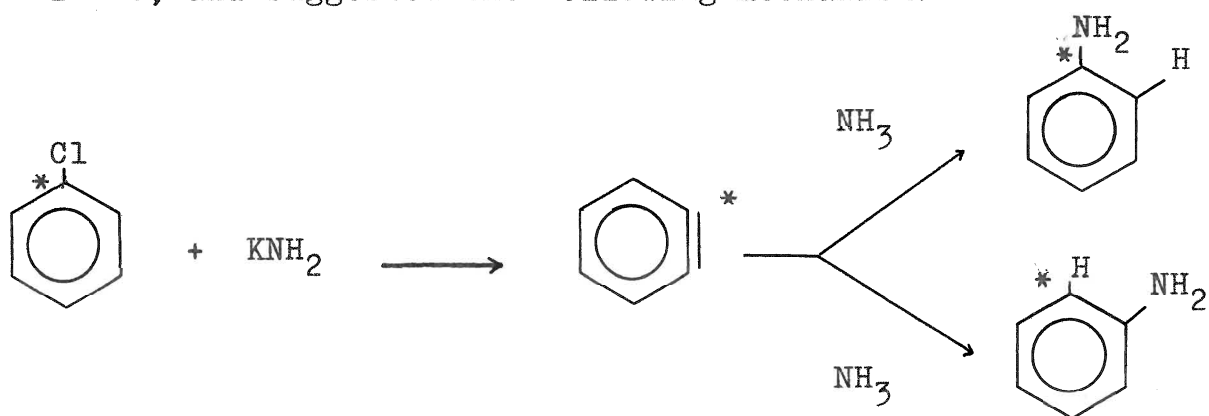
When an electronegative entity is attached to a benzene ring, the 2-hydrogens become the most acidic. If various benzene derivatives (such as fluorobenzene, trifluoromethylbenzene, and methoxybenzene) are deuterated and treated with potassamide in liquid ammonia, exchange is found to be fastest at the 2-position and slowest at the 4-position. Deuterobenzene and deuterotoluene<sup>3</sup> exchange too slowly for convenient measurement. This work is one of the best demonstrations of acidity of such hydrogen atoms.

If the electronegative group present is a halogen, then the 2-halogenophenyl anion, formed by loss of a proton, may lose halide ion, to give a benzyne.



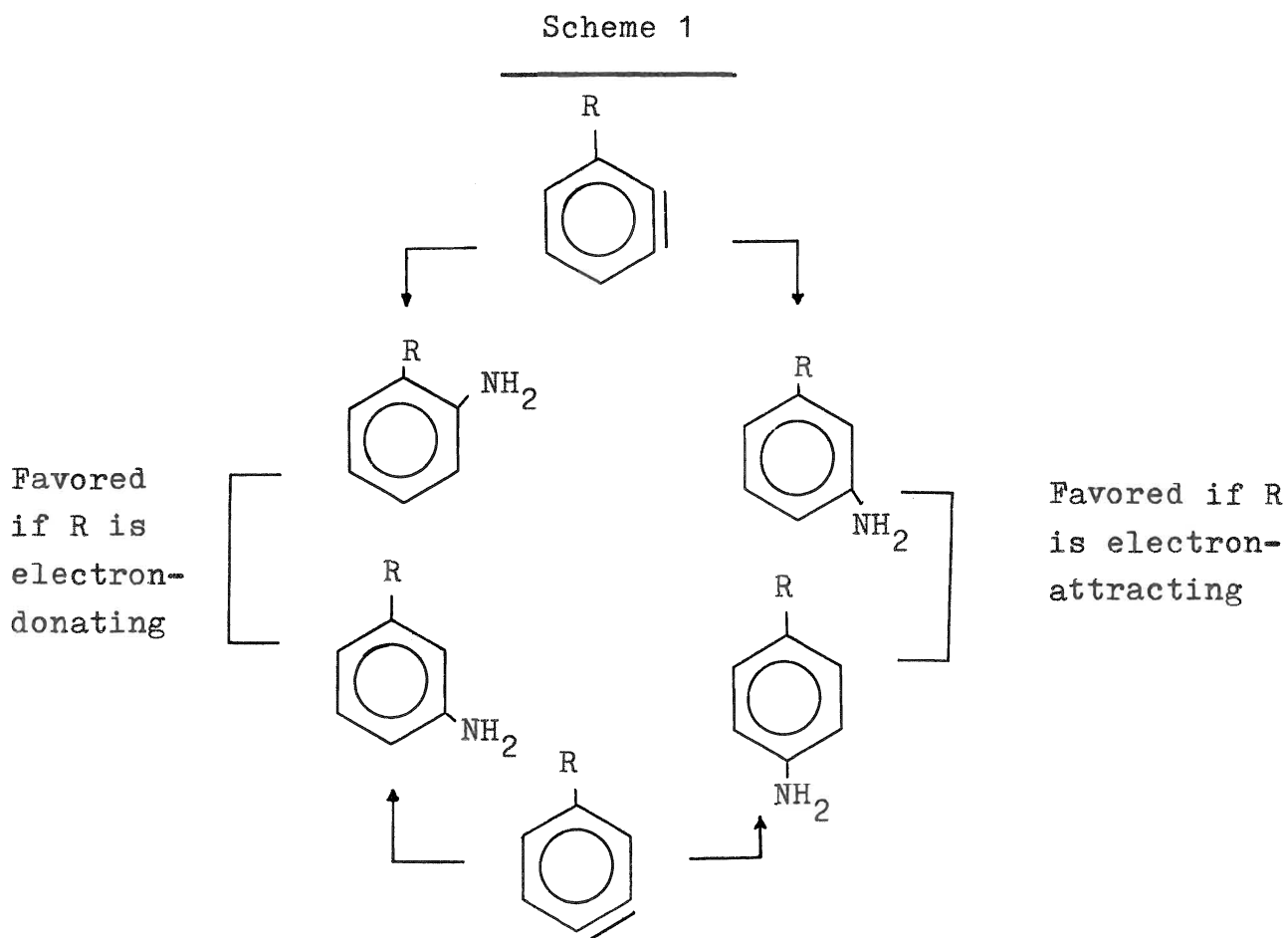
The benzyne, once produced, can react with nucleophiles. In 1953, Roberts and coworkers<sup>4</sup>, who put the benzyne hypothesis on the road to general acceptance, have reported that the phenyl halides (except fluorobenzene) react with potassamide in liquid ammonia to form aniline. They further showed that chlorobenzene

$^{14}\text{C}$  gives nearly equal amounts of aniline- $^{14}\text{C}$  and aniline- $^{14}\text{C}$ , and suggested the following mechanism:

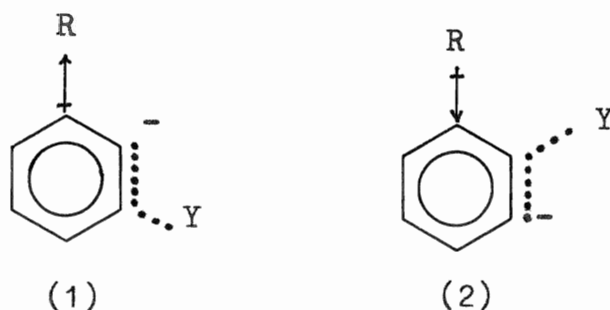


The slight difference from a 1:1 product ratio was of the magnitude and direction expected of a  $^{12}\text{C}/^{14}\text{C}$  isotope effect.

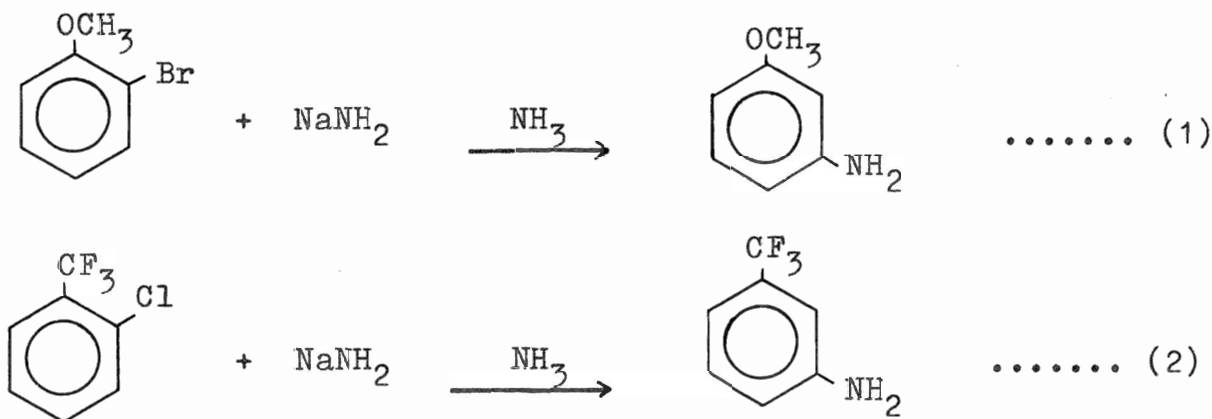
Furthermore, Roberts and co-workers<sup>5</sup> proposed (Scheme 1) that the inductive effect of the substituent controlled the direction of addition of the amide ion to a 3-substituted aryne.



When the 3-substituent is inductively electron-withdrawing, as both  $\text{OCH}_3$  and  $\text{CF}_3$  are, transition state (1) for addition at the more remote position would be favoured because the negative charge is localised on a carbon adjacent to the substituent. The alternate transition state (2) is favoured when the substituent R- is a methyl group (both ortho and meta products are obtained), which is consistent with this interpretation.



Typical examples of such orientation had been reported earlier by Bergstorm and Gilman<sup>6</sup> (equations 1-2):

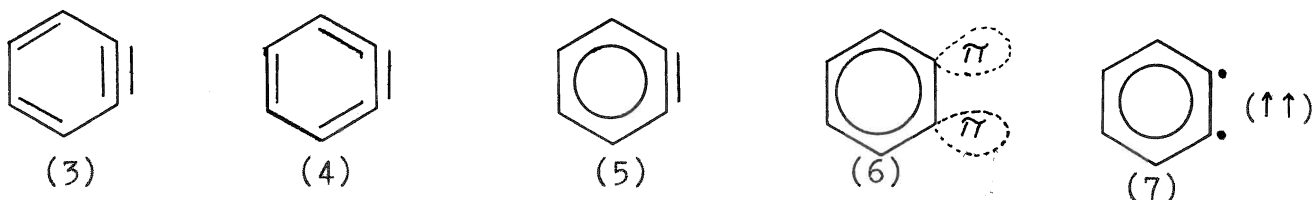


Such Cine-substitution in reactions involving arynes is sometimes useful synthetically, for example, in making some amines that would be difficult to make in other ways. The nitro group is a well known powerful electron-withdrawing group, and when attached to a benzene ring, the 2-hydrogens should become more acidic even than the 2-hydrogens in aryl halides.



It is surprising, therefore, that possible aryne formation from aromatic nitro-compounds has not apparently been examined.

Five formula types suggested for benzyne are (3) to (7).



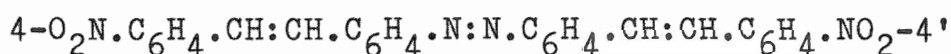
In the current literature, formula (3) is the one most widely found, but this unfortunately represents only one contributing structure of benzyne; another, (4), is rarely explicitly mentioned. Use of formula (3) alone thus leads the reader to neglect (4) and implies the presence of a "triple" bond in benzyne.

As the resulting bond order from equal contributions of (3) and (4) would be 2.5, a full triple bond is definitely absent. In reality benzyne contains a nearly unperturbed aromatic system and a weak extra bond in the orthogonal plane. This state is best represented by formula (5), which circumvents many difficulties encountered with (3), (4), and (6). Formula (5) will therefore be used throughout this thesis. None of the other formulae shows that the aromatic  $\pi$ -cloud and the extra  $\pi$ -bond are placed orthogonally, and only (6), which was suggested by Roberts and his co-workers<sup>5</sup>, implies that the extra bond does not necessarily have a full bond order. However, in the current literature, formula (6) has been discontinued in order to achieve uniformity.

It has now been established unequivocally that benzyne can exist for definite periods of time in the gaseous state. It has been also suggested<sup>7</sup> that benzyne is produced in the form of the biradical (7). This has been discussed recently<sup>2</sup> in detail.

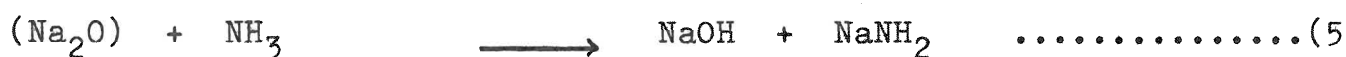
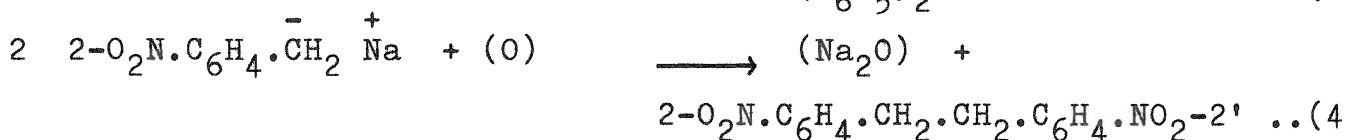
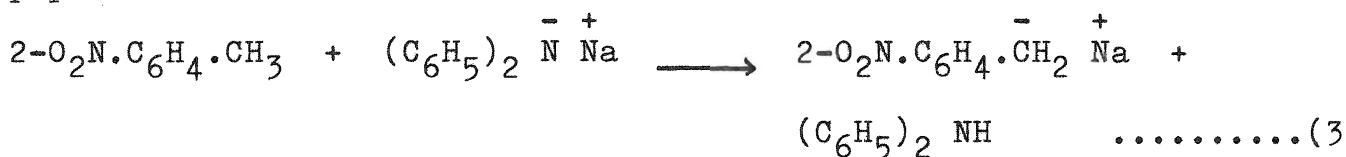
(II) The oxidative coupling of 2-, and 4-nitrobenzyl compounds in strong basic medium

The prolonged treatment of 2-, and 4-nitrobenzyl compounds by strong base has<sup>long</sup> been recognized to give products in which the methylene group has been oxidized and the nitro-group possibly reduced. Perkin first noted the formation of insoluble material from the action of hot alcoholic potassium hydroxide on 4-nitrotoluene<sup>8</sup>. Klinger<sup>9</sup> obtained red amorphous and insoluble materials from reduction of 4-nitrotoluene with sodium in methanol. Bender and Schultz<sup>10</sup>, in a reinvestigation of this work, were able to show that 4,4'-diaminostilbene could be obtained by reduction of the amorphous product described by Klinger. Fischer and Hepp<sup>11</sup> were able to isolate 4,4'-dinitrobibenzyl and 4,4'-dinitrostilbene from the reaction of 4-nitrotoluene with sodium methoxide in methanol. However, the major product was a compound of empirical formula  $C_7H_5NO$ . Green<sup>12</sup> suggested the following structure for this compound ( $C_{28}H_{20}N_4O_4$ ).



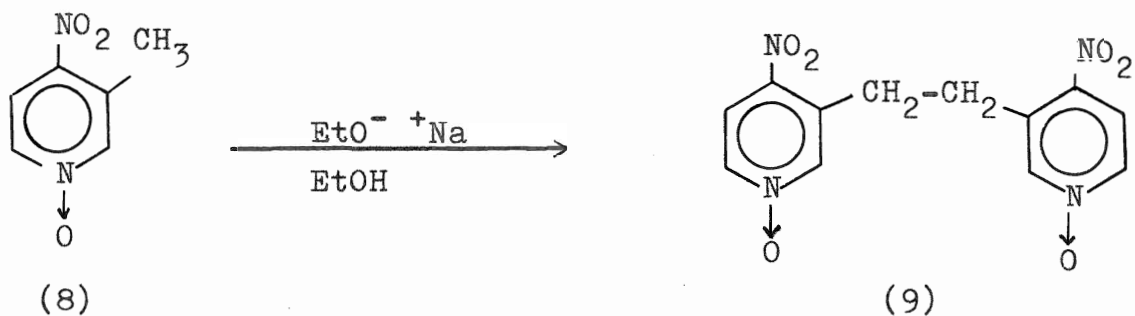
Numerous 2,2'-disubstituted 4,4'-dinitrobibenzyls or stilbenes have been prepared by treating the appropriate 2-substituted-4-nitrotoluene with methanolic potassium hydroxide in the presence of an oxidizing agent<sup>12</sup>.

2,2'-Dinitrobibenzyl has been isolated from treatment of 2-nitrotoluene with diphenylamine anion in liquid ammonia solution<sup>13</sup> (equations 3-5). Similarly 4,4'-dinitrobibenzyl was formed from 4-nitrotoluene with this base or with sodamide in piperidine<sup>14</sup>.

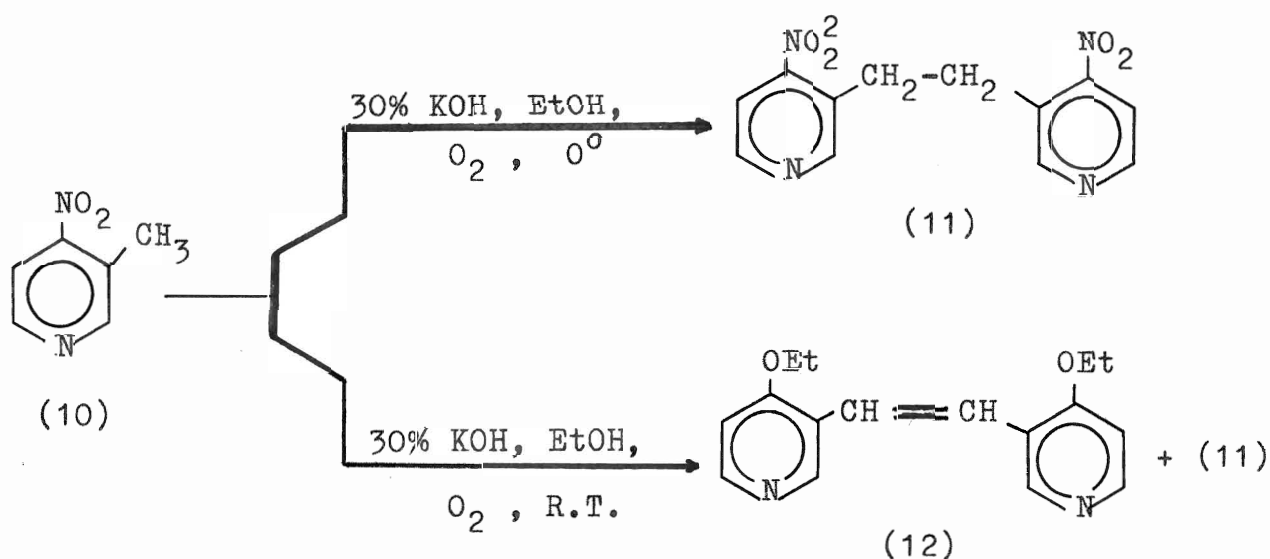


The oxidative coupling of nitrotoluene and its derivatives in basic solution is not an isolated phenomenon. It can be expected in basic solution whenever hydrogen atoms are  $\alpha$  to an easily reducible group that also promotes the acidity of the hydrogen atoms.

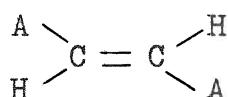
In 1961, Taylor and Driscoll reported<sup>15</sup> that 4-nitro-3-picoline-1-oxide undergoes oxidative coupling when treated with sodium ethoxide in the absence of external oxidizing agents. Since they recovered unchanged 4-nitro-3-picoline(10) under similar conditions, they concluded that the N-oxide group rather than the 4-nitro group is the effective oxidizing agent in the conversion of (8) to (9). However, treatment of (10) with 30% potassium hydroxide in ethanol in the presence of oxygen at room temperature



yields 1,2-di(4'-ethoxy-3'-pyridyl)ethylene (12) ; Taylor and Driscoll shown that (11) is an intermediate in this conversion.



This type of behaviour is not limited to nitro-compounds. Similar reactions have been noted with various alkylquinones.<sup>16</sup> For example, 2-methylanthraquinone is reported<sup>16</sup> to react with ethanolic potassium hydroxide at 150-170° to give 1,2-di(anthraquinon-2-yl)ethylene (13a). The structure has been confirmed later<sup>17</sup> by spectroscopic measurements. It has been suggested also that it is the trans isomer<sup>17</sup>.

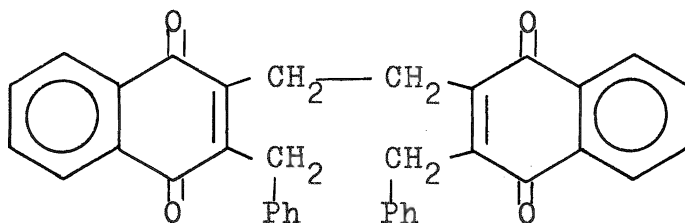


(13a), A = anthraquinon-2-yl (yield, 84%)<sup>17</sup>

(13b), A = anthraquinon-1-yl (yield, 20%)<sup>17,18</sup>

Scholl and Wallenstein have reported<sup>18</sup> that 1-methyl-anthraquinone reacts with potassium hydroxide and sodium acetate at 165° to give 1,2-di(anthraquinon-1-yl)ethylene(13b).

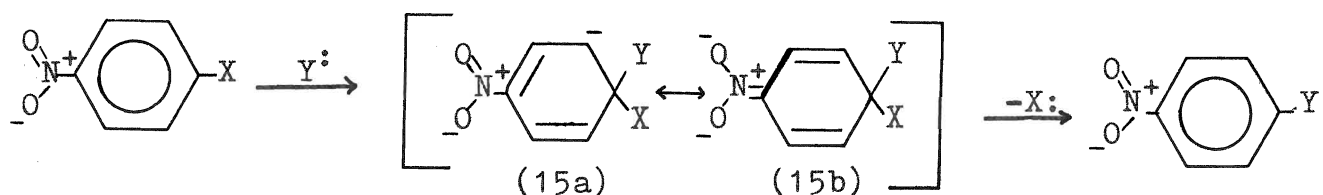
Several oxidative coupling reactions of a similar type have been reported. For example, 3-benzyl-2-methyl-1,4-naphthoquinone reacts with aqueous ethanolic sodium hydroxide to give the dimer (14)<sup>19</sup>, and methyl-4-methylbenzoate reacts with potassium t-butoxide in t-butyl alcohol-dimethylsulphoxide in the presence of air to give 4,4'-bis-methoxy carbonyl stilbene<sup>20</sup>.



(14)

(III) Replacement of hydride ion from aromatic nitro-  
compounds by nucleophiles.

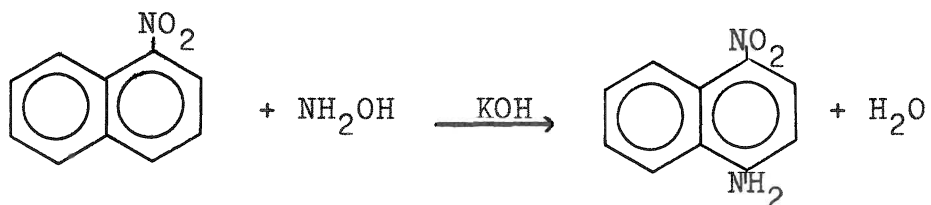
Nucleophilic substitution reactions in aromatic systems are well known reactions. A nitro-group ortho-, or para- to the position under attack facilitates the reaction by dispersing the negative charge brought in by the attacking group before departure of the leaving group ( $15a \longleftrightarrow 15b$ ).



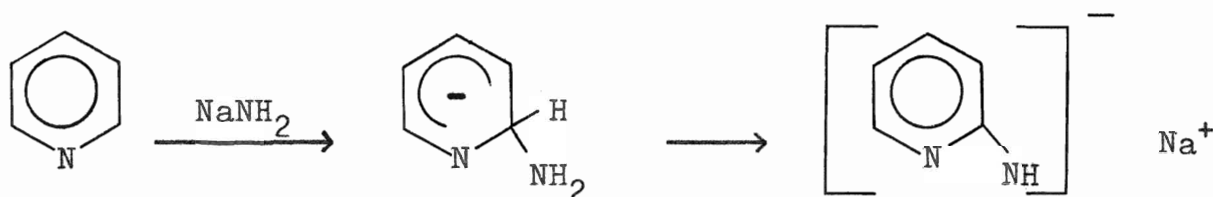
Fewer examples of replacement of hydride ion from aromatic nitro-compounds are available. Good examples are the oxidation of nitrobenzene to 2-nitrophenol by the action of potassium hydroxide in air<sup>21</sup>, the formation of N-(4-nitrophenyl)carbazole from nitrobenzene and potassiocarbazole<sup>22</sup>, and the formation of p-nitrophenyl piperidine, 4-piperidino-1-nitronaphthalene, and X-piperidino-8-nitroquinoline upon treatment of 4-nitrobenzene, 1-nitronaphthalene, and 8-nitroquinoline, respectively, with sodiumpiperidide<sup>23</sup>.

Further typical cases of hydride displacement in aromatic, and heterocyclic compounds are illustrative.

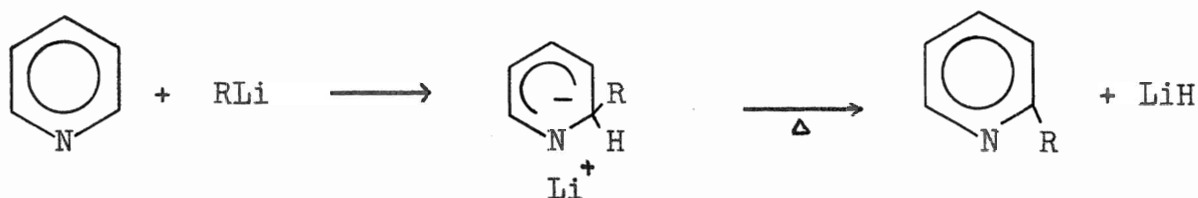
Amination by hydroxylamine<sup>24</sup>. Reactive aromatic compounds can be directly aminated with hydroxylamine, in the presence of strong bases.



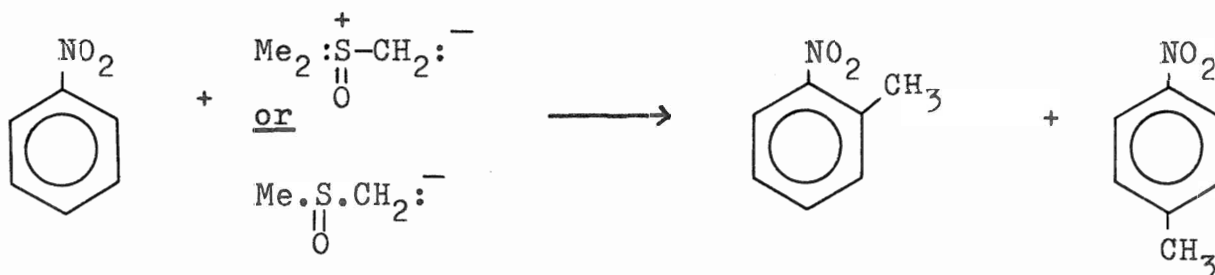
Amination of heterocyclic nitrogen compounds. Pyridine and other heterocyclic nitrogen compounds can be aminated with alkali-metal amides, in a process called the Chichibabin reaction<sup>25</sup>. The attack is always at 2-position to the nitrogen, unless both positions are filled, in which case attack at 4-position occurs. Nitro-compounds do not give the reaction.



Alkylation and arylation of heterocyclic nitrogen compounds with alkyl, and aryllithiums<sup>26</sup>. The reaction occurs by an addition-elimination mechanism.



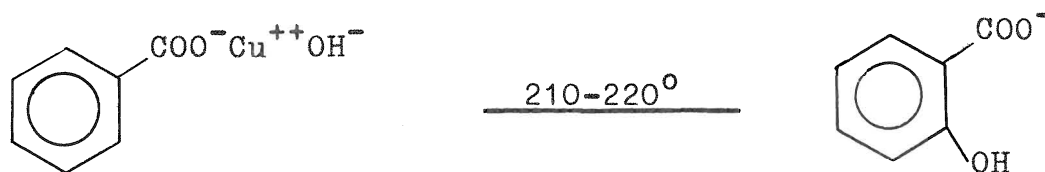
Methylation of aromatic nitro-compounds by treatment with dimethyloxosulfonium methylide<sup>27</sup> or the methyl sulfinyl carbanion (obtained by treatment of dimethyl sulfoxide with a strong base<sup>28</sup>).



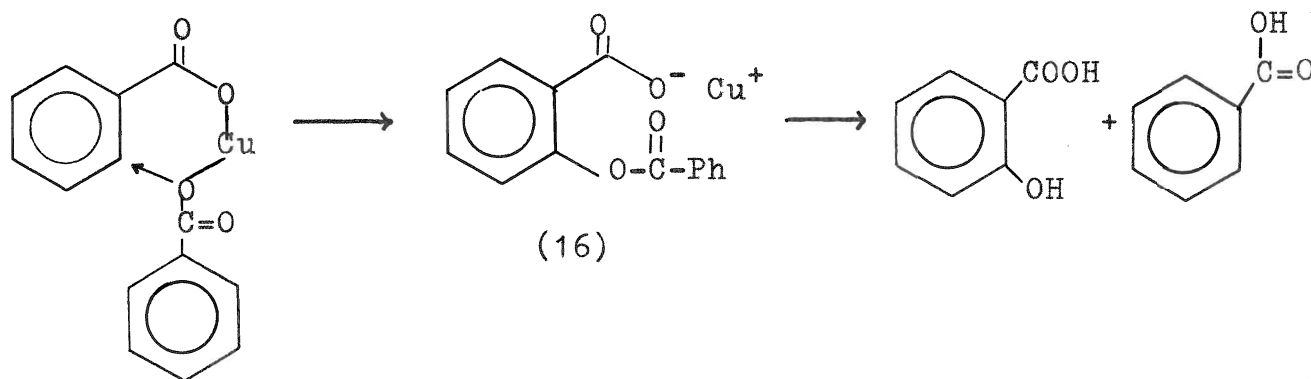
(29,30)

Hydroxylation of aromatic acids

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When basic copper salts of aromatic acids are heated, hydroxylation occurs in the ortho position<sup>29</sup>. Better results are<sup>30</sup> obtained by heating cupric carboxylates in protic solvents.



In the later case there is a cyclic process leading to an ester intermediate(16). The author has proved that cupric ion, present as the salt of benzoic acid, was the oxidizing agent for the production of salicylic acid.

The aspects of aryne chemistry, nucleophilic substitution, and oxidative coupling reactions described above bear directly on the objectives of the research described in this thesis. These objectives were: (i) to investigate the feasibility of useful amination reactions of various aromatic nitro-compounds via aryne intermediates or by direct nucleophilic substitution, and (ii) to investigate the feasibility of coupling various alkyl-aromatic nitro-compounds to give bibenzyl and stilbene derivative, by use



of potassamide in liquid ammonia.

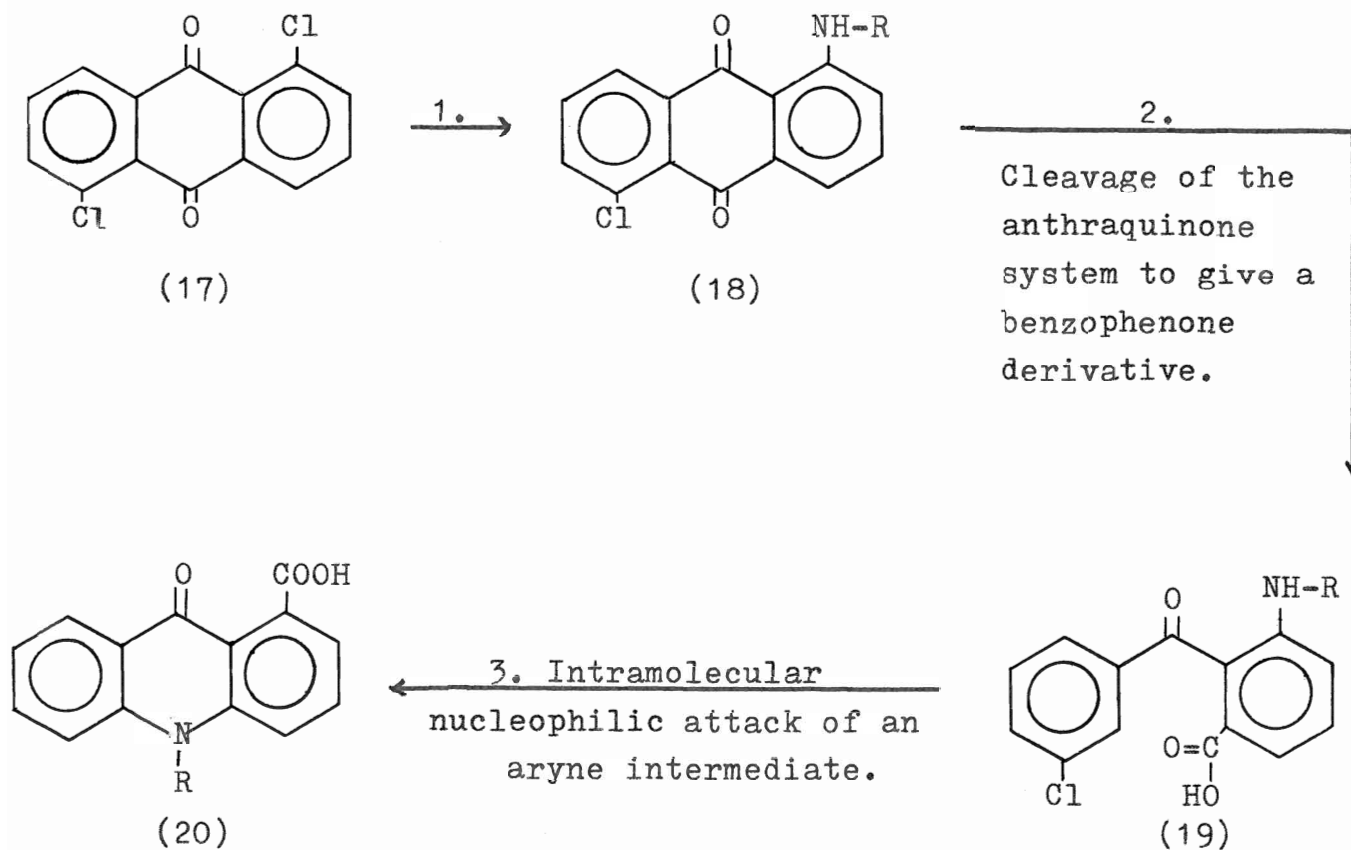
## Section (II)

The treatment of selected anthraquinones and related compounds with formamide and N-methylformamide.

### Introductory comment.

The route to acridone derivatives explored in this thesis is summarized in the following scheme (Scheme 2).

### Scheme (2)

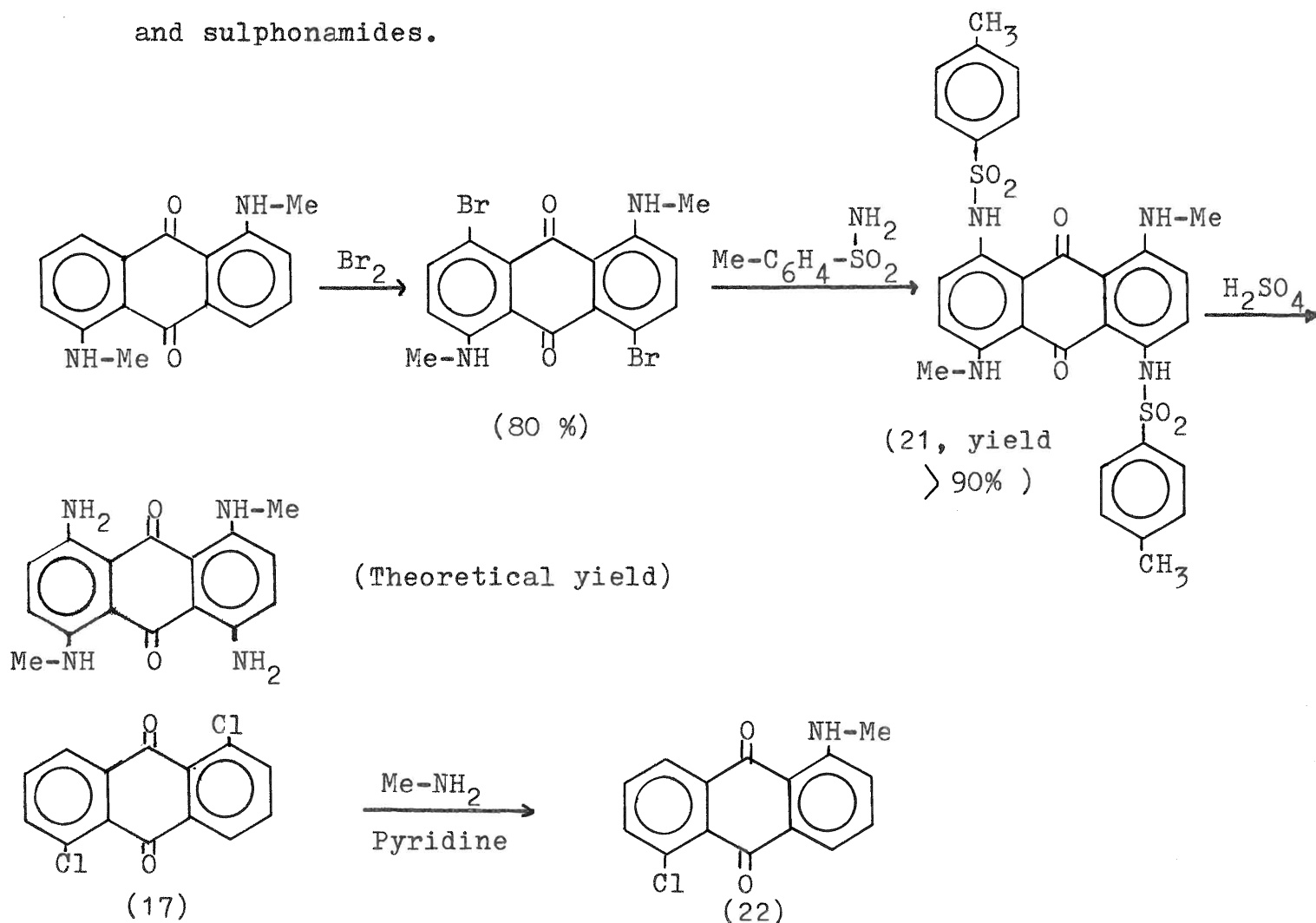


Processes for displacement of halogen in halogeno-anthraquinones by nitrogen-containing nucleophiles (step 1), for cleavage of the anthraquinone system (step 2), and for effecting ring clo-

sure via aryne intermediate (step 3) are illustrated below.

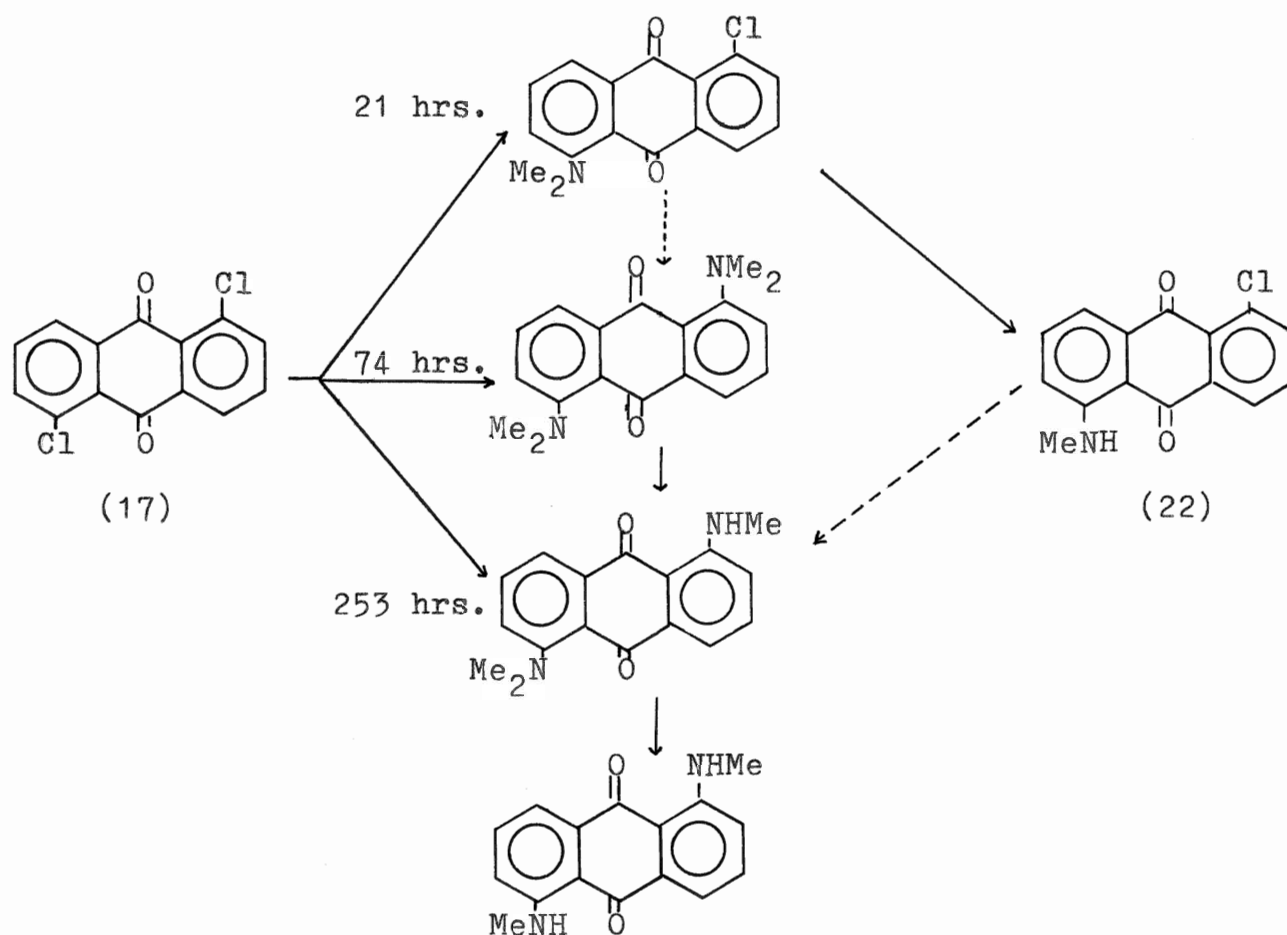
(i) Introducing amino groups into the reactive  
halo-anthraquinone system

In 1948, Hall and Hey reported<sup>31</sup> syntheses of (21) and (22) by reactions involving the use of 4-toluenesulphonamide and of methylamine respectively as nucleophiles. These are typical of many reactions of halogen-containing anthraquinones with amines and sulphonamides.



Dimethylamino-anthraquinones have been prepared from halo-  
geno-anthraquinones using N,N-dimethylformamide as reagent.  
The recent report of Lord and Peters<sup>32</sup> on this reaction notes  
the formation of N-methylaminoanthraquinones in some cases when

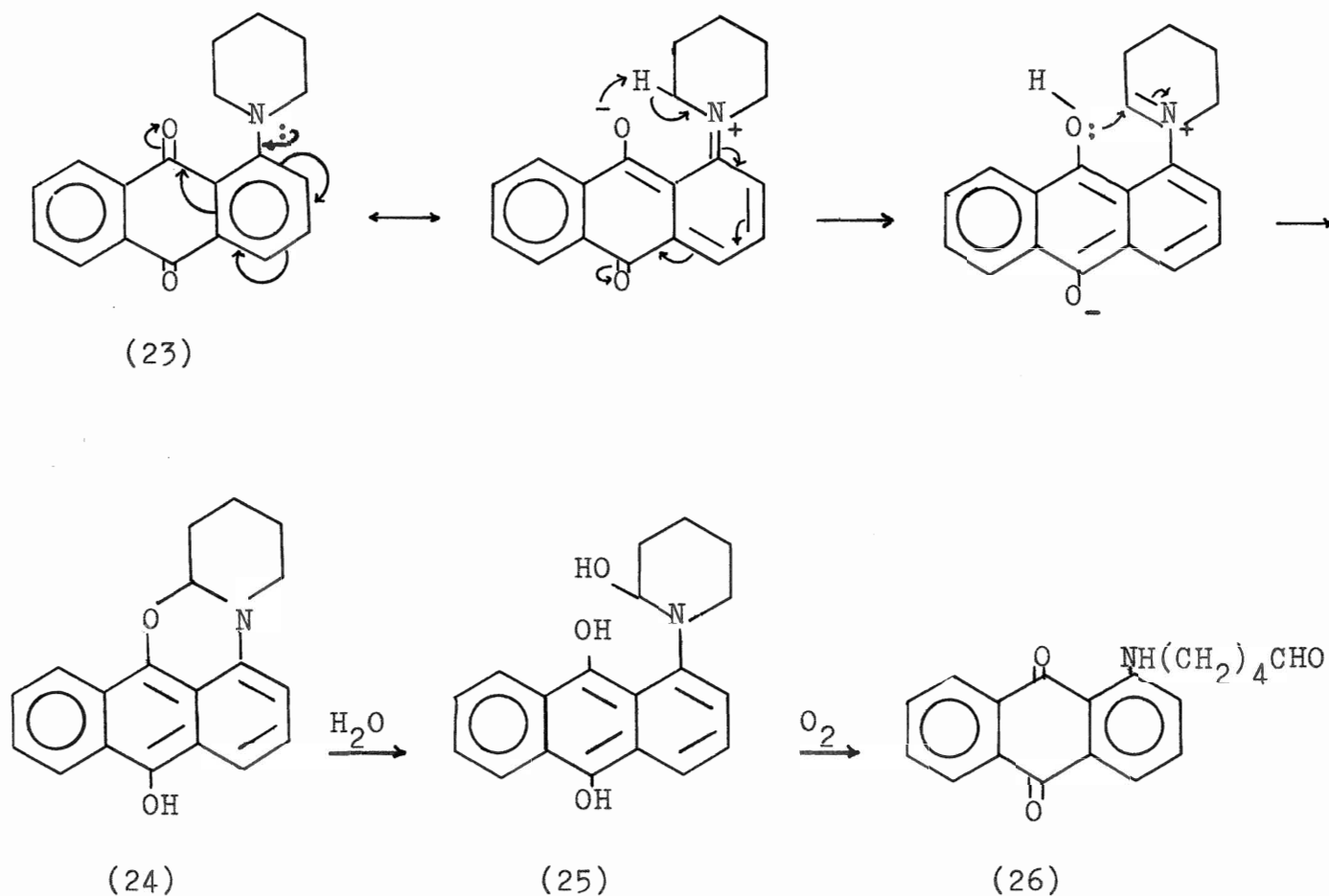
the reaction time is prolonged (Scheme 3); this reaction thus affords examples of normal and anomalous halogen replacements. The authors did not offer an explanation of this novel demethylation. Such demethylation was observed in the reactions of 1-chloro-, 1,2-, 1,4-, 1,5-, and 1,8-dichloroanthraquinones with dimethylformamide, but no demethylation occurred when 2-chloroanthraquinone was treated with dimethylformamide for 105 hours under the same conditions.



(Scheme 3) Products isolated from the reaction between 1,5-dichloroanthraquinone and DMF<sup>32</sup>.

Fokin and his co-workers<sup>60</sup> had previously observed dealkylation of various 1-dialkylaminoanthraquinones on heating at 160-190° in pyridine, a reaction originally reported by Bradley and his co-workers<sup>61</sup>. The Russian group extended this reaction to cyclic 1-aminoanthraquinones such as the piperidino-derivative (23, Scheme 4), and again observed ring opening to give the aldehyde (26)<sup>62</sup>, which they showed was formed by way of the intermediates (24) and presumably (25) since (24) could be trapped as its acetate on treatment of the reaction mixture with acetic anhydride<sup>63</sup>. The reaction has been recently explained by Lynch and Meth-Cohn<sup>33</sup> in terms of the mechanism shown in Scheme 4.

(Scheme 4)<sup>33</sup>



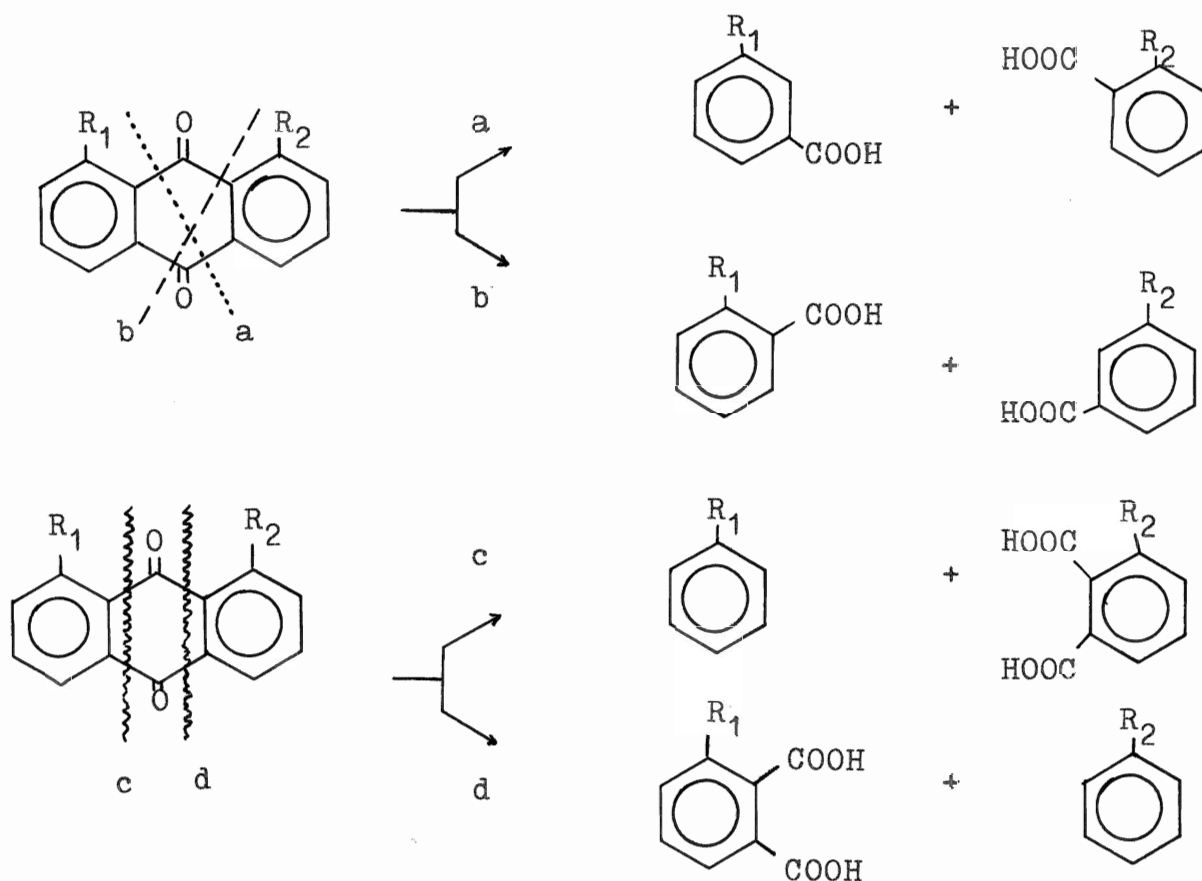


1-hydroxyanthraquinone (5.9%) and 1-aminoanthraquinone (37.8%) were obtained in addition to the anticipated 1-(4-pyridylamino)-anthraquinone.

(ii) Cleavage of some anthraquinones  
upon treatment with base.

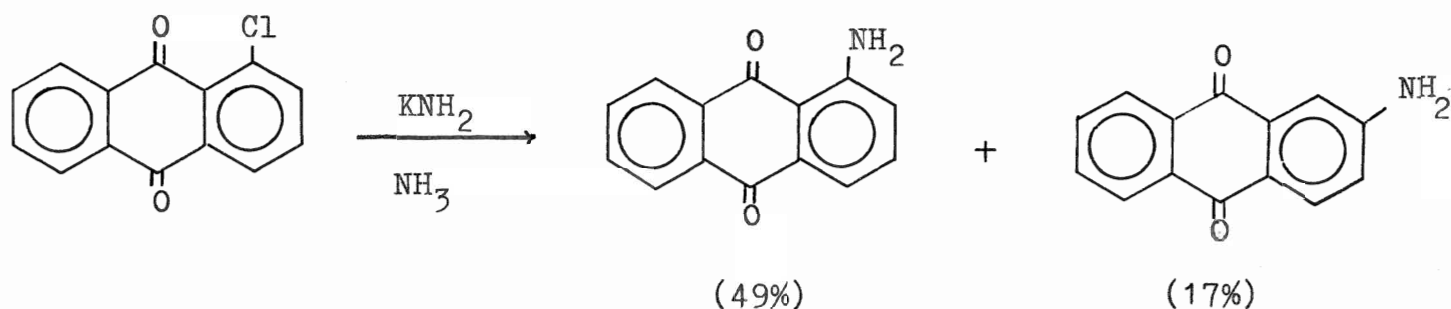
Despite the fact that anthraquinones are more resistant to cleavage by base than many other types of non-enolizable carbonyl compounds, Davies and Hodge in 1971 reported<sup>34</sup> the successful cleavage of anthraquinone, several methoxyanthraquinones, and 1-, and 2-chloroanthraquinones in high yield to afford mixtures of (substituted) benzoic and/or phthalic acids by treatment with an excess of potassium t-butoxide-water reagent in 1,2-dimethoxyethane at ca. 85°. Anthraquinones can, in principle, be cleaved in four ways by this reagent (Scheme 6)<sup>34</sup>. 1-Chloroanth-

Scheme (6)



raquinone gave under these conditions a mixture of benzoic acid (23%), 3-chlorobenzoic (32%), and phthalic acid (45%) of the acid fraction (90-96%) obtained. 2-Chloroanthraquinone gave an acid fraction (97%) containing 39% of benzoic, 39% of mixture of 3-chlorobenzoic and 4-chlorobenzoic, and 22% of phthalic acids.

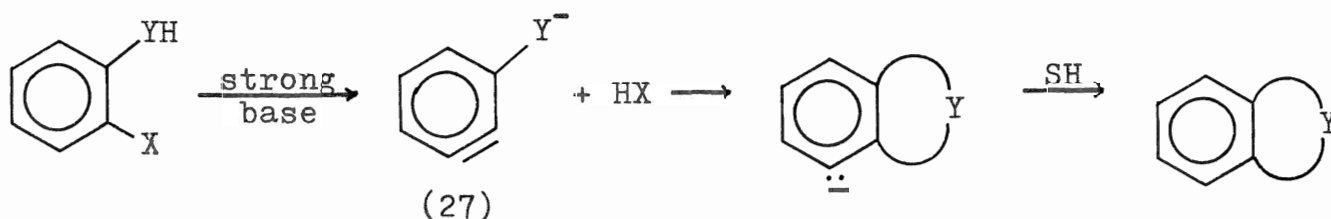
However, when 1-chloroanthraquinone was treated with potassiumamide in liquid ammonia, no significant cleavage was observed<sup>35</sup>; instead, the main products were 1-, and 2-aminoanthraquinones. 2-Chloroanthraquinone was recovered in 82% yield under these conditions<sup>35</sup>.



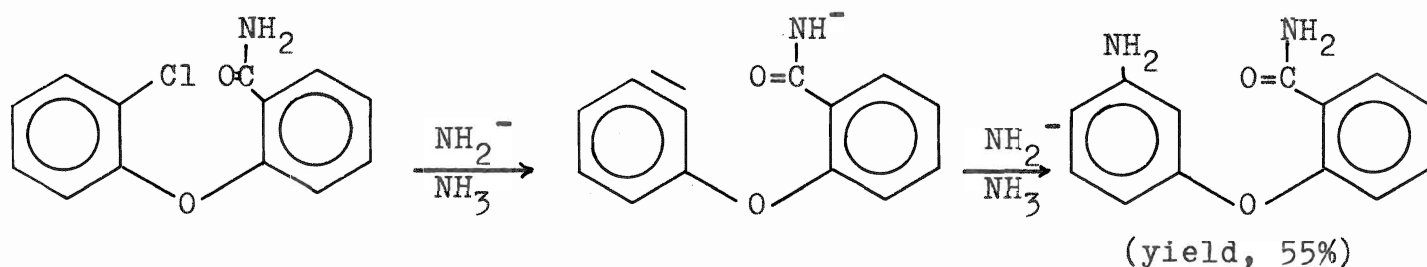
### (iii) Ring closure via aryne intermediates

The main objective in such ring closures is to create an intermediate, such as (27) in scheme 7, which has both an aryne and a strong nucleophile suitably located in a side chain. The nucleophile can then add intramolecularly to the aryne, and finally a proton will be acquired (scheme 7).

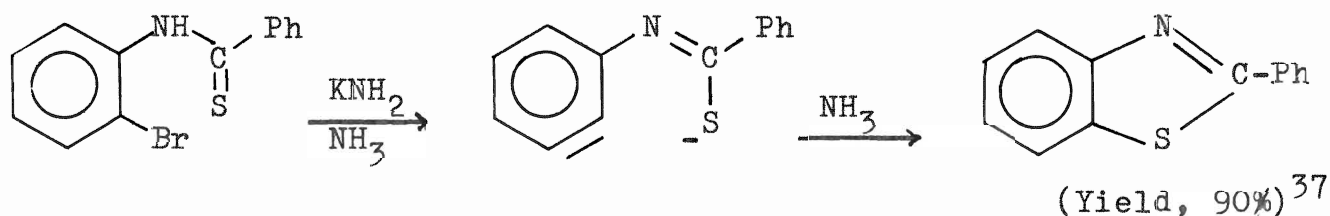
#### Scheme (7)



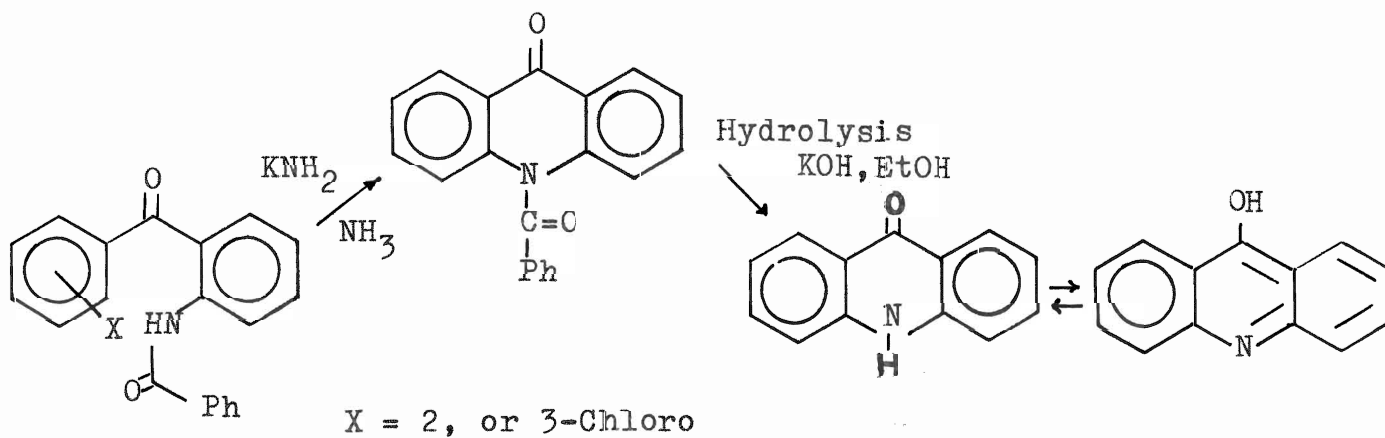
A difficulty with the scheme is that the side chain nucleophile may not be an effective competitor with the external base, i.e. the intermediate is sometimes attacked by the external base, rather than by the side chain nucleophile. The following is a typical example<sup>36</sup>.



The side chains involved in such ring closures have included carbon, oxygen, nitrogen, and sulphur as the nucleophilic atom. Several new syntheses of ring systems, including benzothiazoles and indoles, were developed using this approach (37, 38, 39).



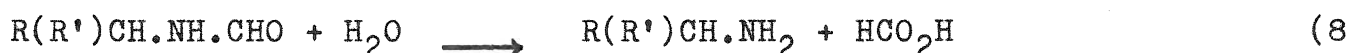
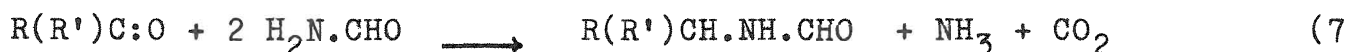
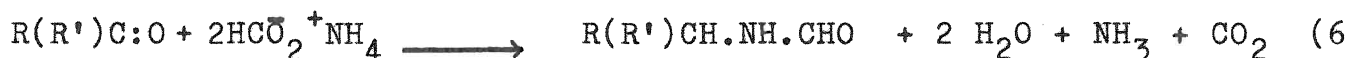
Recent work<sup>35</sup> that has not yet been published in the literature, reports a synthesis of acridone using this technique as shown below.





(iv) The Leuckart reaction

It is interesting that formamide has not been used to introduce amino-groups into anthraquinones by nucleophilic displacement of halogen, possibly because of fears of alternative Leuckart reactions involving the carbonyl groups. The reaction may be illustrated for ketones by the following equations.

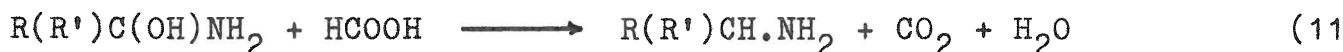


Leuckart<sup>40</sup> discovered the reaction in an attempt to prepare benzylidenediformamide,  $C_6H_5.CH(NH.CHO)_2$ , by heating benzaldehyde with formamide, but the reaction gave benzylamine and its formyl derivative, dibenzylamine and its formyl derivative, and tribenzylamine. Ammonium formate was found to react in the same way as formamide.

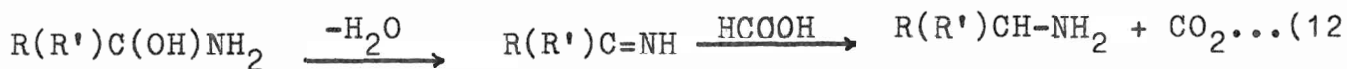
A single mechanism capable of accounting for all the variations of the Leuckart process can be postulated on the basis of the decomposition of the formamide, by hydrolytic or thermal means, respectively to formic acid and ammonia or an amine.



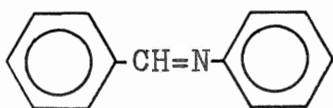
The base so formed may then react with the carbonyl compound to give an addition product which is reduced by formic acid to an amine; reaction of this amine with more formic acid leads to the salt or the amide. This mechanism was originally proposed by Wallach<sup>41</sup> and outlined in equations 10-11.



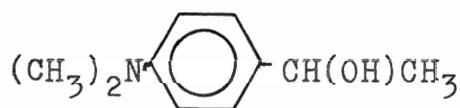
It has also been suggested that an alternative path for primary and secondary amines might involve the reduction of an intermediate imine and imonium respectively<sup>42</sup>.



Alexander and Wildman<sup>43</sup>, conducted experiments to determine how such intermediates would behave. As a model imine, benzal-aniline (28) was chosen, but as ketone ammonias are unstable, for they have selected 4-dimethylaminophenylmethylcarbinol (29) as an alternative for study. Benzalaniline and 4-dimethylaminophenylmethylcarbinol were reduced to N-benzylaniline (97%) and 4-dimethylaminoethylbenzene (6%) respectively by heating with triethylammonium formate, 50 % HCOOH + (CH<sub>3</sub>.CH<sub>2</sub>)<sub>3</sub>N, at temperatures ranging from 130° to 160°, but boiling with 90% formic acid led to the formation of resinous materials.

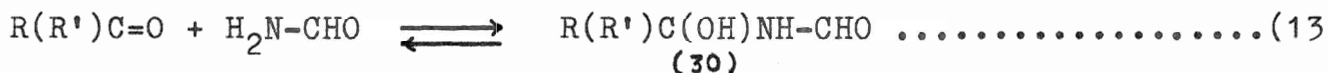


(28)



(29)

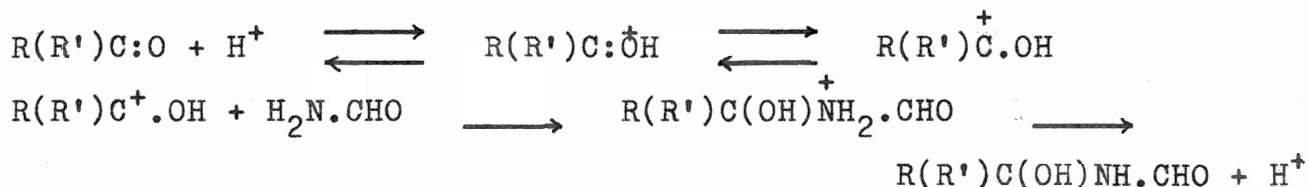
Doever and Courtois<sup>44</sup> and Davies and Rogers<sup>45</sup> suggest that in the reaction between ketones and formamide, the first reaction is the addition of formamide to the carbonyl group (equation 13).



A compound of the same type as (30), R(R')C(OH)NH-CHO, is reported by Shive and Shive<sup>46</sup>; they isolated α-hydroxy-α-formaminopropionic acid on mixing pyruvic acid with formamide at 40°. These investigators agree that the first step is the

formation of a carbon-nitrogen bond between the carbon atom of the carbonyl group, and the nitrogen atom of ammonia or formamide. This is then followed by the reduction of the hydroxy compound thus formed by means of formic acid or formamide, respectively.

The catalytic effects observed by Webers and Bruce<sup>47</sup> are in agreement with the proposed mechanism. The reaction between benzophenone and formamide is catalyzed by ammonium formate, ammonium sulfate, or magnesium chloride, and it has been suggested by these authors that the catalyst polarizes the carbonyl group and thus facilitates the addition of formamide or ammonia. The

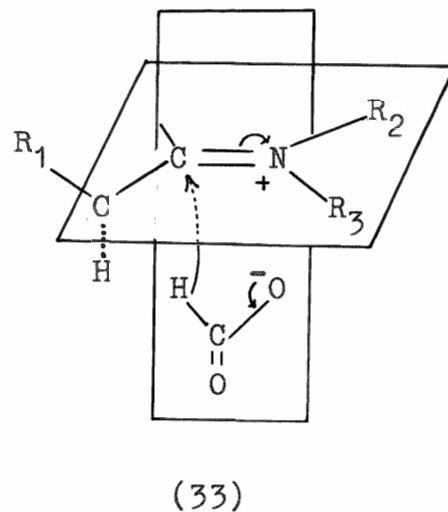
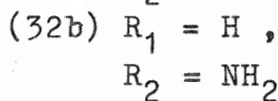
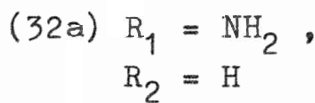
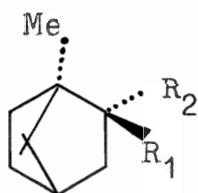
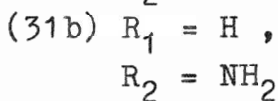
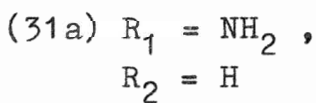
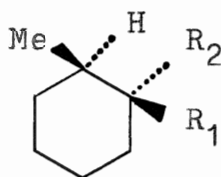


function of an ammonium salt as a catalyst for the reaction is probably to furnish a proton from a complex in equilibrium with its dehydration product, the amide. The magnesium chloride, or its reaction product with formamide,  $\text{Mg}(\text{HN.CHO})_2$ , or magnesium ion could coordinate with the oxygen atom of the carbonyl group.

The stereochemical course of the Leuckart reaction is apparent from a number of examples. Thus camphor<sup>48</sup> gave 70% isobornylamine (neobornyl)(31a) and 30% of bornylamine (31b). Menthone is reported to give a somewhat more complex mixture containing about 65% of neomenthylamine (32a), about 25% of menthylamine (32b), and smaller percentages of iso- and neoiso-menthylamine.<sup>49</sup> Isomenthone gives a very similar mixture<sup>50</sup>. Ingersoll has very carefully characterized the mixtures of amines resulting from thujone<sup>51</sup> and from fenchone<sup>52</sup>. Leuckart reaction of 2-phenoxy-

cyclohexanone with some secondary amines has been shown<sup>57</sup> to give mixtures containing 71-77% of the corresponding Cis 2-phenoxy-cyclohexylamines.

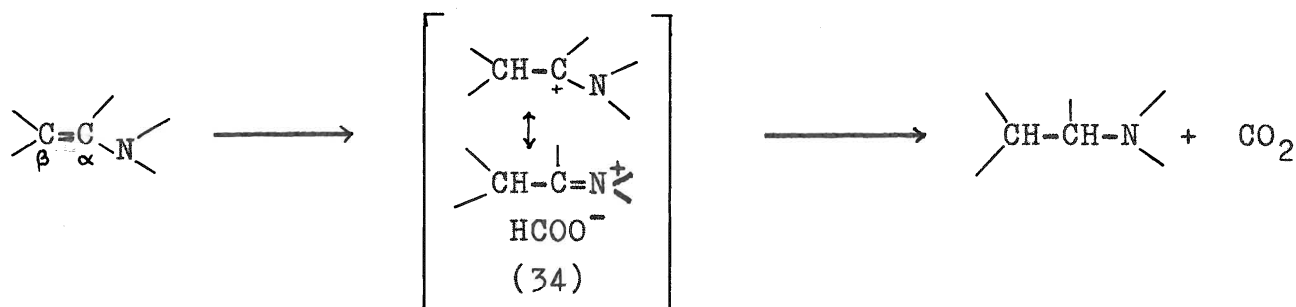
These results are all consistent with the postulate that predominant addition of hydrogen occurs from the relatively unhindered side of the molecule leading to the formation of the "more cis" amine. However, in 1952, Noyce and Bachelor<sup>52</sup> studied the stereochemical specificity of the Leuckart reaction and suggested that the critical step in the reaction is the formation of an activated complex (33) with the orientation of the formate ion conditioned by the dipolar attraction of the immonium ion. These



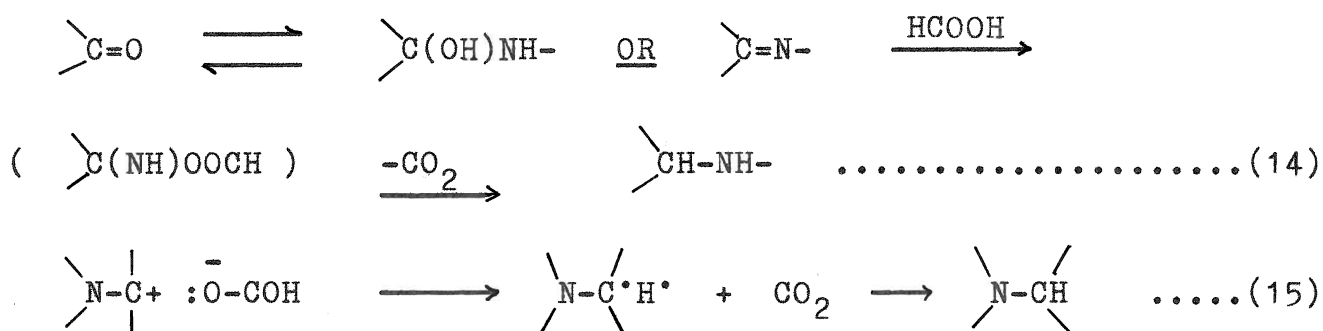
investigators have carried out the reaction on 2-methylcyclohexanone to give a mixture of the cis- and trans-2-methylcyclohexylamines (cis > trans).

More recently, Leonard and Sauers<sup>53</sup> have studied the course of formic acid reduction of enamines by means of deuterium-labeled formic acid (DCOOH, HCOOD, DCOOD); the process is related to the Leuckart reaction<sup>54</sup>. These investigators agree with the

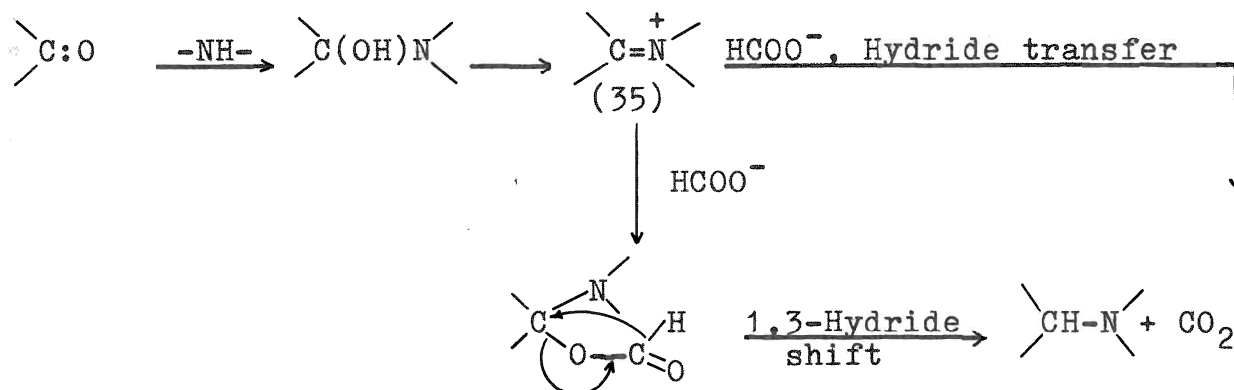
suggestion of Noyce and Bachelor and propose that a ternary iminium grouping such as (34) is involved as intermediate in the reaction and that addition of hydrogen occurs from the relatively less hindered side of the intermediate.



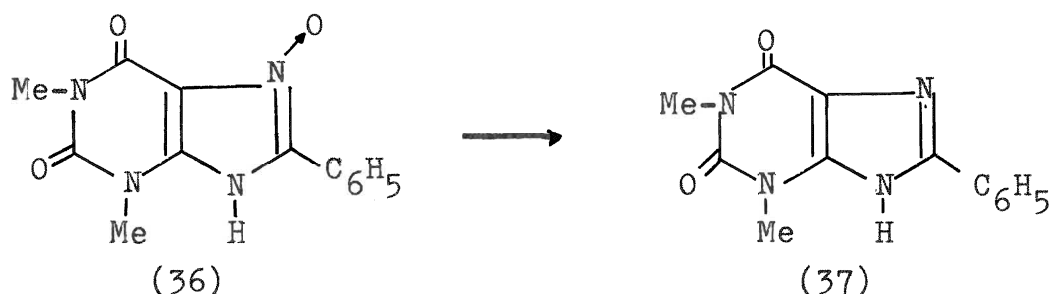
Lukasiewicz<sup>55</sup> has suggested that the reducing action of formic acid probably occurs via the formation of an ester (equation 14) and has produced evidence to suggest that the decarboxylation of this ester to give the alkylated amine is a free-radical process (equation 15).



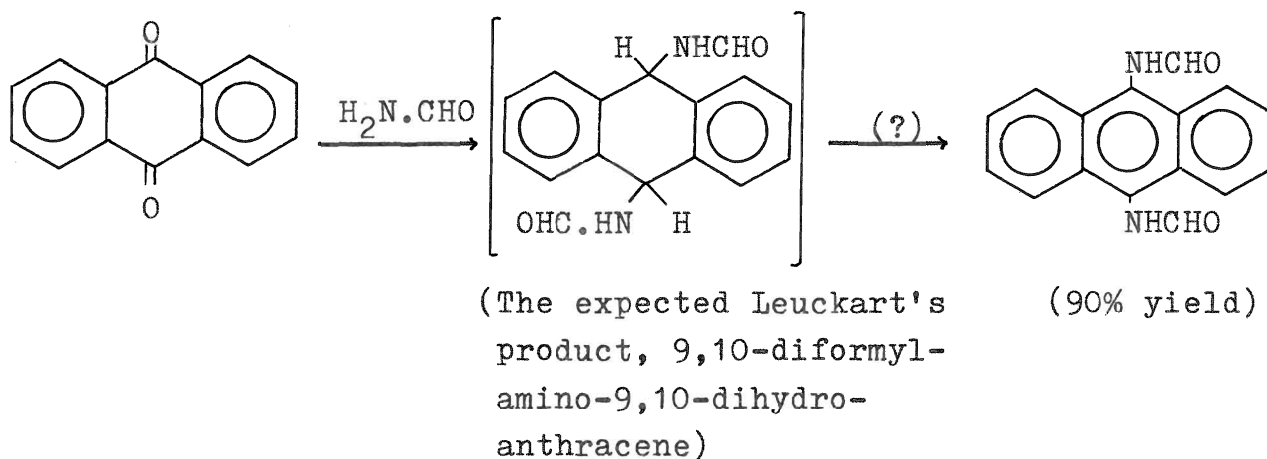
More recently Coe and Uff<sup>57</sup> have proposed a reasonable mechanism for the Leuckart reaction for secondary amines which involves the immonium ion (35).



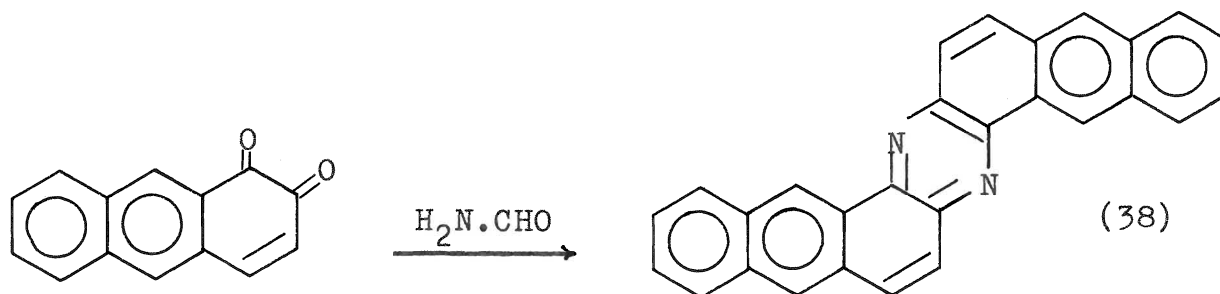
In 1964, Taylor and Garcia reported<sup>58</sup> the first example of the participation of N,N'-dimethylformamide alone as the reducing agent in a Leuckart-type reaction. Heating the N-oxide (36) in N,N'-dimethylformamide results in the evolution of dimethylamine and the formation of (37).



p-Quinones are also reported to undergo the Leuckart reaction<sup>56</sup>; for example, the N,N'-diformyl derivative of 9,10-diamino-9,10-dihydroanthracene is reported in "Organic Reactions" as the product from reaction of formamide with 9,10-anthraquinone. This report is incorrect; reference to Schiedt's original paper identifies this product as the N,N'-diformyl-derivative of 9,10-diaminoanthracene but the author did not offer an explanation for the aromatization step (Scheme 8).

Scheme (8)

o-Quinones, on the other hand, give the corresponding pyrazines. Thus, 1,2-anthraquinone is converted to bis-ang-di-anthracenopyrazine (anthrazine, 38).



The initial objective of this part of the work was <sup>to</sup> examine the feasibility of a synthesis of 1-carboxyacridone derivatives from 1,5-dichloroanthraquinone. Development of this project provided a focus for examining the reaction of various anthraquinones and related compounds with formamide and has led, as are result, to a new process for converting anthraquinones to the corresponding anthracenes.

## DISCUSSION

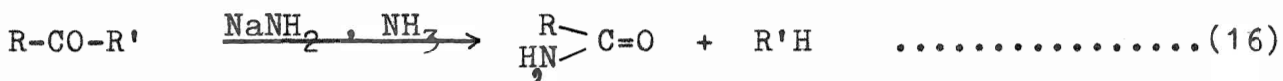


## SECTION (I)

### TREATMENT OF AROMATIC NITRO-COMPOUNDS WITH POTASSAMIDE IN LIQUID AMMONIA

#### 4-NITROBENZOPHENONE

Just prior to this work, Vines<sup>64</sup> had been studying the Haller-Bauer reaction (equation 17):



Vines had treated 4-nitrobenzophenone with potassamide in liquid ammonia for 4 hours and identified two products, namely benzoic acid resulting from Haller-Bauer scission and X-amino-4-nitrobenzophenone resulting from hydride displacement by amide ion.

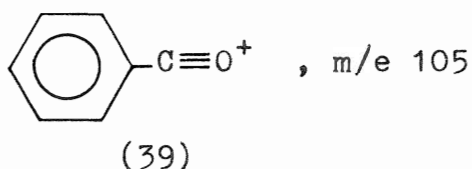
The present work began, therefore, with consideration of the following questions:

(1) Was the amination to be found with any other aromatic nitro-compounds ?

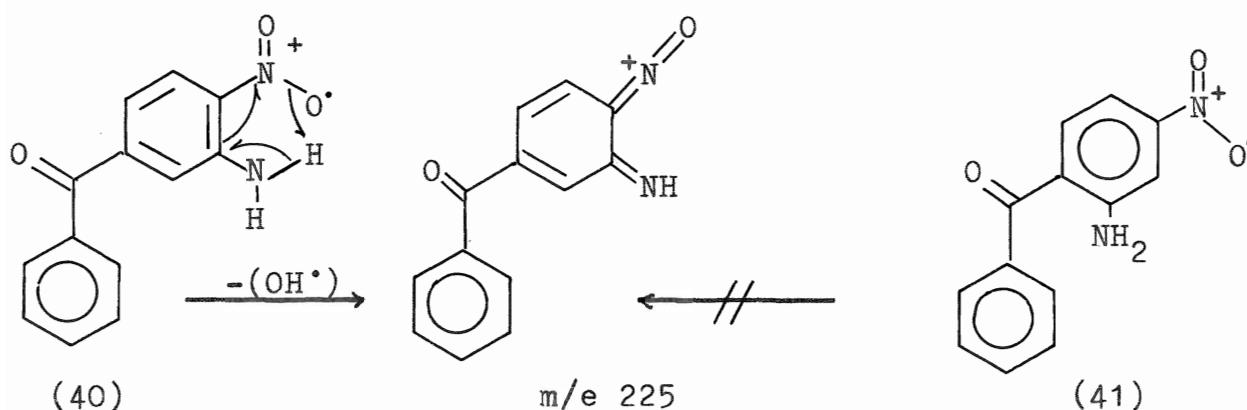
(2) What was the fate of the nitrobenzene produced in the Haller-Bauer reaction ?

In order to answer these questions, it was decided to re-examine this reaction of 4-nitrobenzophenone and then proceed to a series of nitro-compounds. It was hoped that the compound described as X-amino-4-nitrobenzophenone was in fact 3-amino-4-nitrobenzophenone, since at present there is no alternative method for the preparation of this compound reported in the literature. Attempts were first made to improve the yield (36%), for example, by increasing the amide concentration or the reflux time, but without success. However, identification of the compound was undoubtedly confirmed as 3-amino-4-nitrobenzophenone. This conclusion is based on the following evidence:

1. The mass spectrum showed a base peak at  $m/e$  105 (100) corresponding to the ion (39) indicating that the amino and nitro groups are attached to the same benzene ring. Moreover, a fragment



peak at  $m/e$  225 corresponding to a hydroxyl loss suggested that the amino-group is situated at 2-position to the nitro-group, since this did not occur in the case of the other isomer (41).



2. A mixed melting point of (40, m.p.  $202^{\circ}$ ) with an authentic sample\* of (41, m.p.  $172-3^{\circ}$ )<sup>65</sup> was found to be  $147-9^{\circ}$ .

3. The i.r. spectra of these two isomers are different, possibly because of hydrogen-bonding between the amino and carbonyl groups in (41) but not in (40). This evidence is enough to prevent any confusion.

\* The present writer is most grateful to Dr. K. Schofield for sending a sample of 2-amino-4-nitrobenzophenone used in this work.

Also was isolated from the acidic fraction a new hydroxylated compound which, in analogy, was identified from mass spectrometry as 3-hydroxy-4-nitrobenzophenone. The mass spectrum showed a parent peak at  $m/e$  243. It also showed that the hydroxyl-group and the nitro-group were attached to the same benzene ring ( $m/e$  105, 100%). Moreover, a peak at  $m/e$  226 corresponding to the ion (42) was observed, while a peak at  $m/e$  165 corresponding to the ion (43) which usually appears in the spectra of 2-hydroxybenzophenones<sup>79</sup> was not observed. These fragmentation processes are shown in diagram (I).

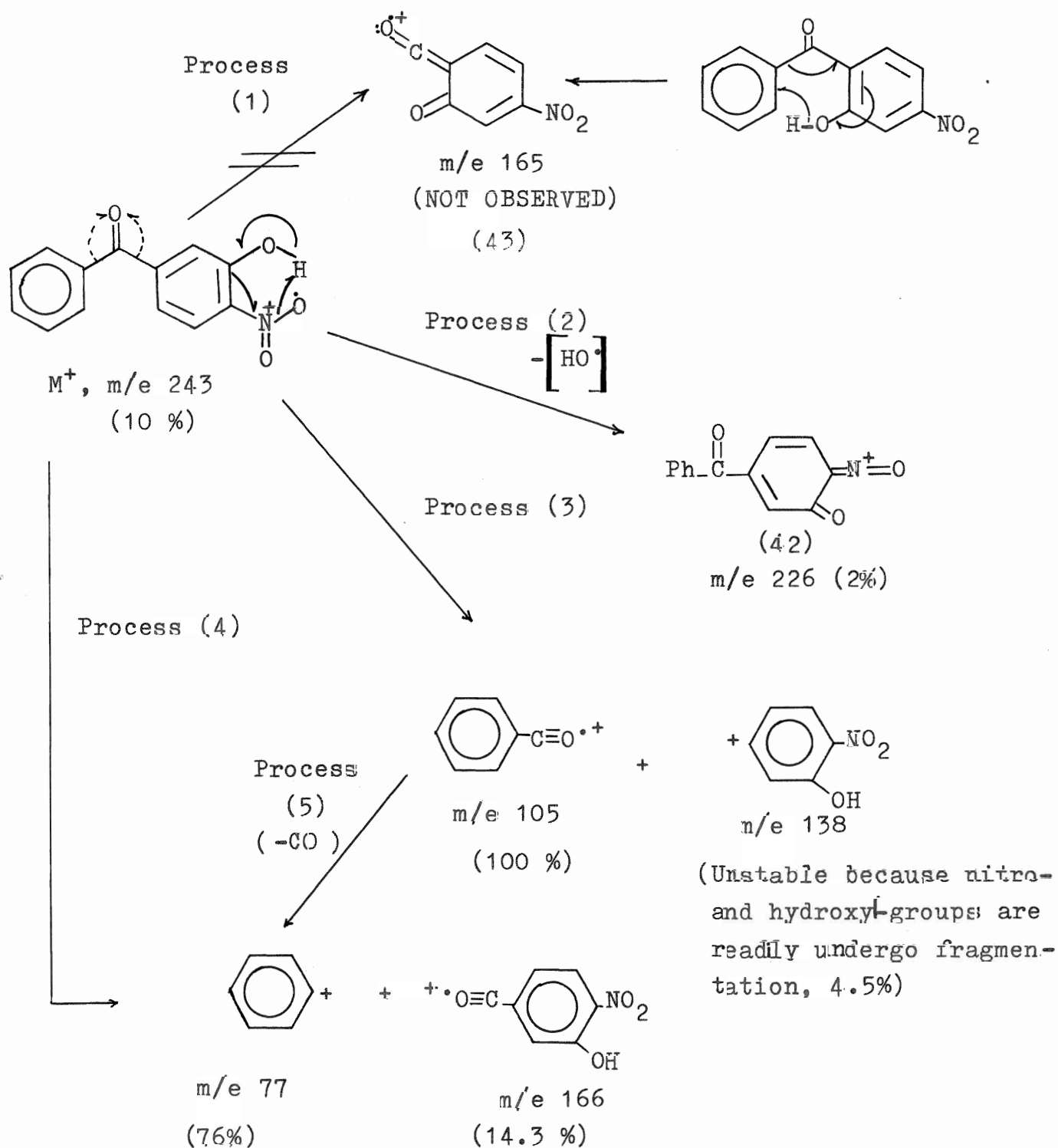
It should be noted in passing that if an aryne was formed in the reaction of 4-nitrobenzophenone with potassamide, 3-amino- and 4-aminobenzophenones should be isolated. However, no evidence for these compounds was obtained.

It seems that the reaction of this aromatic nitro-compound with potassamide involves amination through direct hydride displacement. Other examples of displacement of hydride ion from nitro-compounds by nucleophiles are known, and have been discussed in the Introduction.

#### 4-NITRODIPHENYL SULFONE

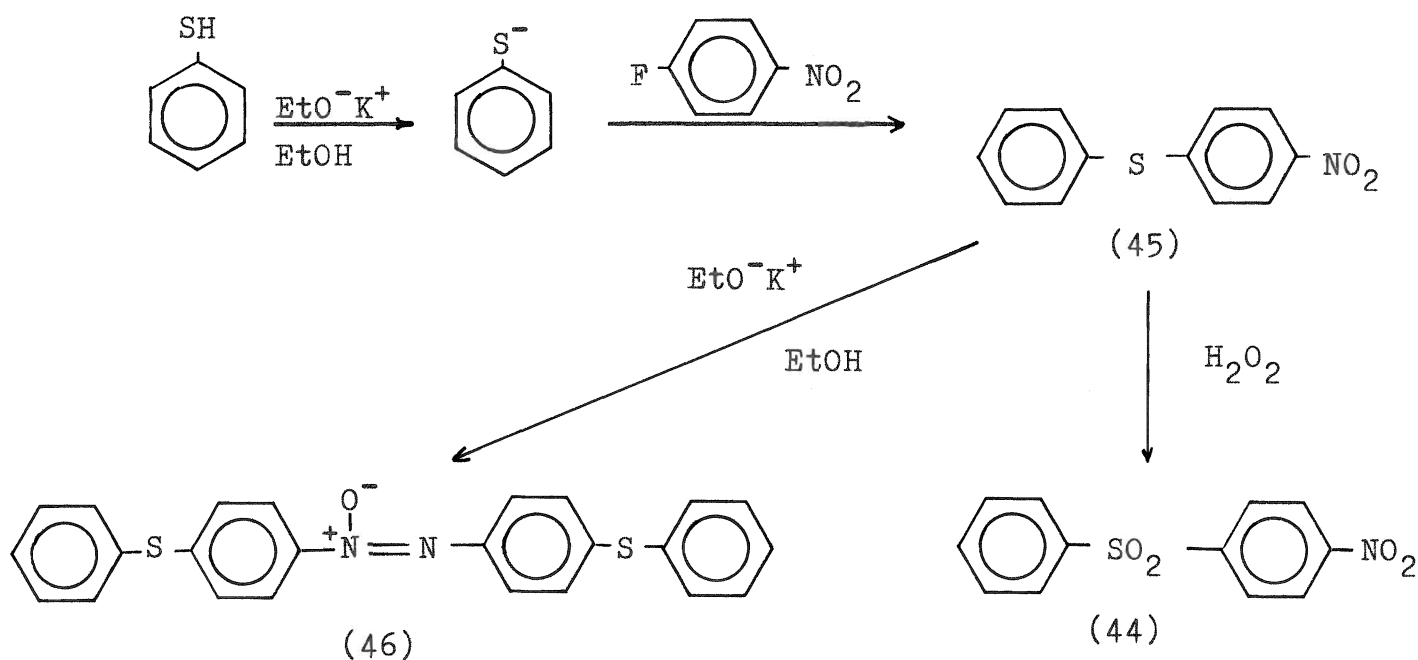
The next compound chosen for examination was 4-nitrodiphenyl sulfone (44). This was prepared by treatment of the corresponding sulfide (45) with hydrogen peroxide solution (30%), a literature method<sup>66</sup>. The sulfide (45) was prepared in 97-99 %

DIAGRAM (I)



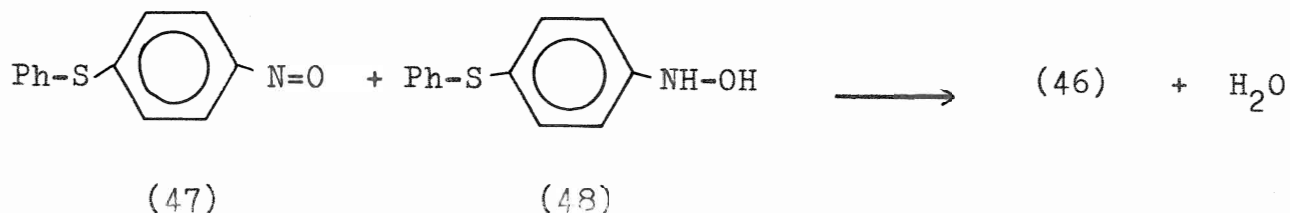
yield by treating 4-fluoronitrobenzene with one equivalent of potassium thiophenolate, prepared from thiophenol and potassium ethoxide in ethanol (Scheme 9). However, when two equivalents of potassium ethoxide were used, only 45.6% of (45) was obtained; a second compound was formed which was identified as a new azoxy compound, 4,4'-di(thiophenoxy)azoxybenzene (46). It is clear

Scheme (9)



that azoxy compound (46) was formed from coupling of two molecules of 4-nitrodiphenyl sulfide (45) in alkaline medium ( $\text{KOEt}$ ), since treatment of (45) with potassium ethoxide in ethanol gave the azoxy compound (46) in almost the same percentage yield. The most probable mechanism is that one molecule of (45) is reduced

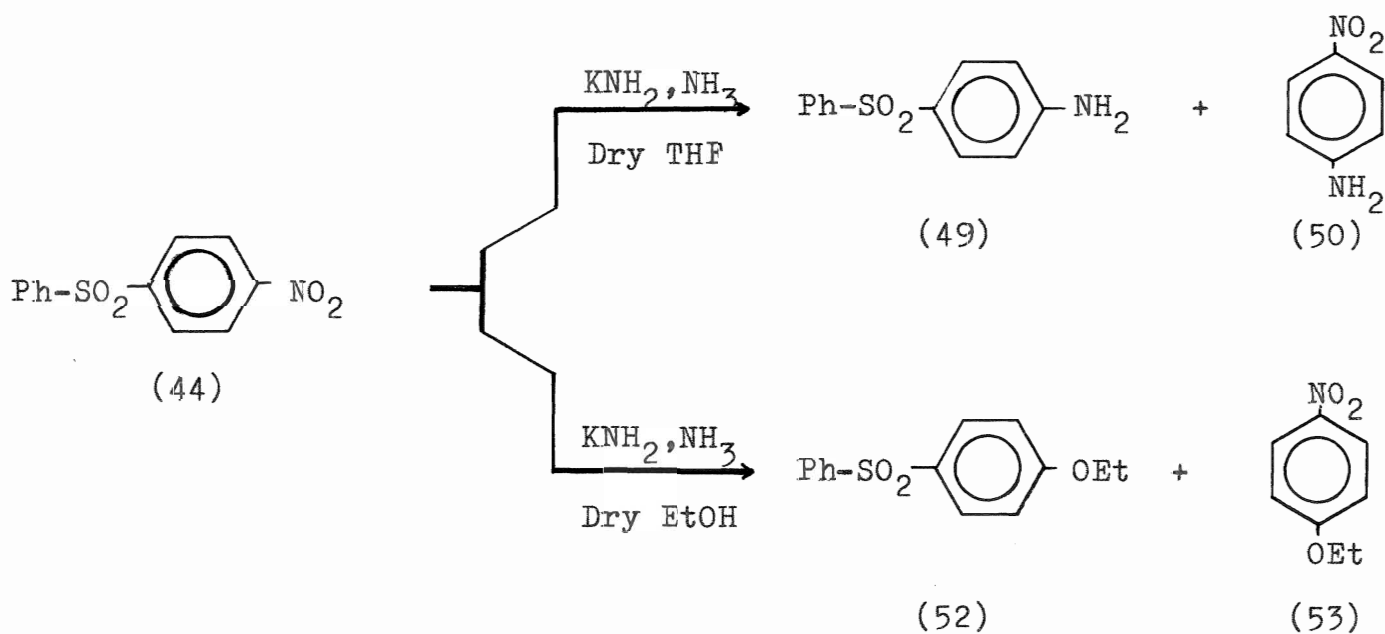
to a nitroso compound (47) and another to a hydroxylamine (48), and these combine:



The mechanism of the combination step is discussed in the literature<sup>30</sup>.

4-Nitrodiphenyl sulfone was dissolved in dry tetrahydrofuran and treated with potassamide in dry redistilled liquid ammonia. Reaction occurred to give 4-aminodiphenyl sulfone (scheme 10, 49, 11%); the presence of 4-nitroaniline (50) was also indicated ( $M^+$ ,  $m/e$  138; same  $R_f$  as an authentic sample of 4-nitroaniline) but this compound could not be isolated in pure condition.

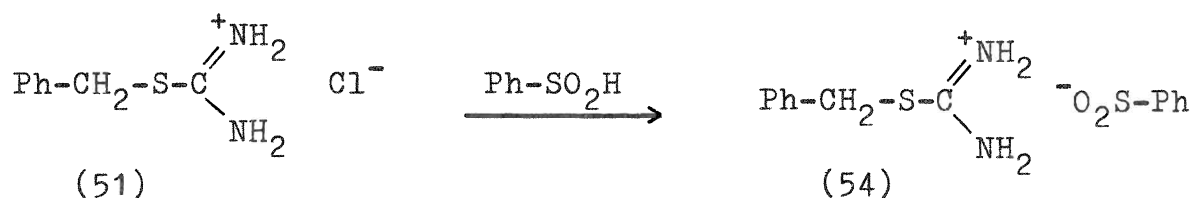
Scheme (10)



Although different procedures for working-up the reaction mixture were used, it was not possible either to isolate more products or to recover any unchanged starting material.

Attempts were particularly made to trap the benzenesulfinate anion (or benzenesulfinic acid) that should be formed along with 4-nitroaniline in the nucleophilic displacement reaction. The aqueous solution produced from washing the reaction mixture with water (see experimental section) was acidified with 4N HCl solution (ph 4), and then treated with a warm (45°) saturated aqueous solution of S-benzylisothiuronium chloride (51)<sup>67</sup>. However, no derivative could be isolated.

In order to examine further the behaviour of (44) towards nucleophiles, it was dissolved in dry ethanol (prepared by a standard method<sup>68</sup>) and treated with potassamide in dry redistilled liquid ammonia under the same conditions. Nucleophilic substitutions were found to have occurred as 4-ethoxydiphenyl sulfone (52, 65%) and 4-ethoxynitrobenzene (53, 29%) were isolated (Scheme 10). A similar attempt to isolate the benzenesulfinate as the S-benzylisothiuronium salt (54) failed. Although this



result shows that nucleophilic substitutions can occur very easily at low temperatures, it was disappointing in that a successful amination of the type noted with 4-nitrobenzophenone was not achieved.

#### 4-NITRODIPHENYL SULFIDE

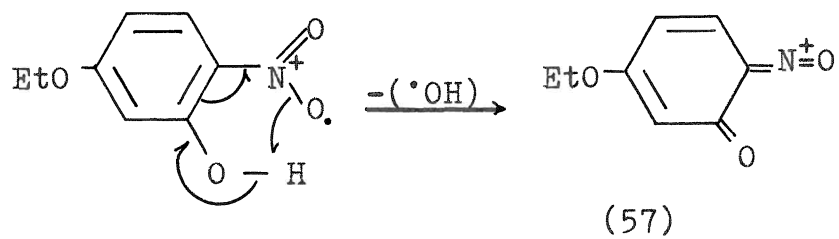
4-Nitrodiphenyl sulfide (45), available from the previous experiments, was next examined. This compound was dissolved in dry freshly distilled tetrahydrofuran and treated with potassamide in liquid ammonia for 4 hours. The reaction mixture was extracted with hot ethanol to give a crude product which contained five components (Thin layer chromatography). The two major components of this mixture were separated by chromatography (Florisil/Benzene).

Surprisingly, ethoxylations were found to have occurred, as 4-ethoxy-2-hydroxynitrobenzene (55) and 4-ethoxynitrobenzene (53) were the products isolated. The position of the ethoxy-group in the former product (55) was assigned 4- to the nitro-group for the following reasons:

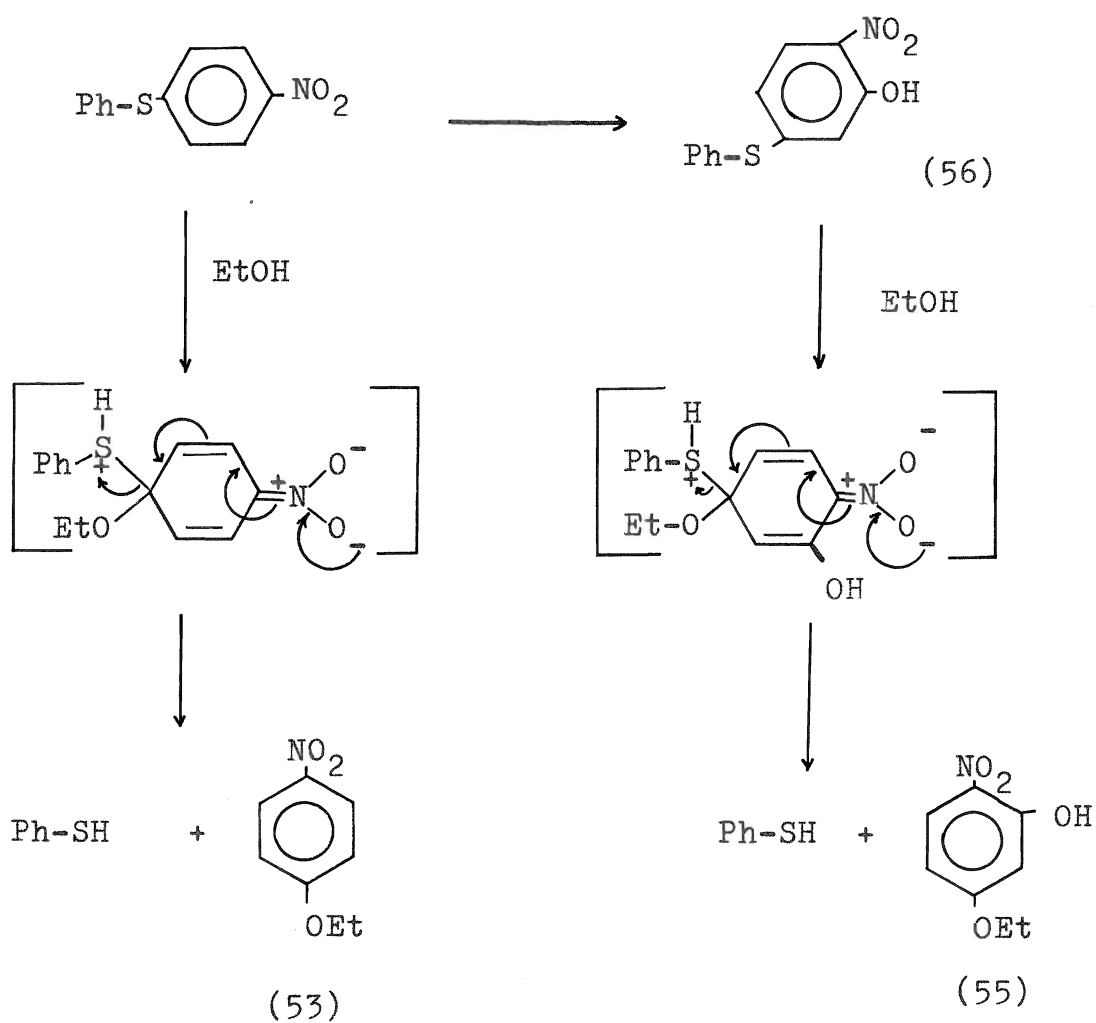
1. It seems reasonable to suppose that ethoxylation has taken place during the final extraction of the reaction mixture, that is after hydroxylation has occurred (Scheme 11).

2. In all examples of nucleophilic replacement of hydride ion from aromatic nitro-compounds reported in the literature or discussed in this thesis, the nucleophile adds at the 2- or 4-position with respect to the nitro-group. By analogy, the hydroxylated product obtained from 4-nitrodiphenyl sulfide should be 3-hydroxy-4-nitrodiphenyl sulfide (56), since the  $C_6H_5-S$ -group occupied the position 4- with respect to the nitro-group. Furthermore, evidence is obtained from the mass spectrum of the product, which shows a fragment peak at  $m/e$  120 corresponding to the ion (57).





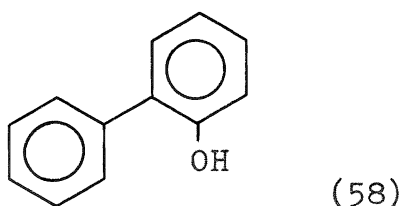
Scheme (11)



## NITROBENZENE

The reaction of nitrobenzene with potassamide was examined in the hope that the absence of this material from the corresponding reaction of 4-nitrobenzophenone would be explained. Also, it was hoped that the products would be easily characterised. Vines showed<sup>64</sup> that nitrobenzene did react under these conditions. He thought that phenol, 2-nitrophenol and 4-nitrophenol were formed, but he was not able to prove this experimentally.

Commercial nitrobenzene was distilled; the mass spectrum indicated, according to mass spectral data<sup>69</sup>, that the distilled sample was pure. Nitrobenzene was then treated with potassamide in liquid ammonia under the normal conditions for 4 hours. Ethanol was used to extract the expected phenols. Thin layer chromatography of the extract showed the presence of six components but three major ones. Mass spectrum of the extract showed parent peaks at  $m/e$  198, 170, 152 and 139 which<sup>were</sup> thought to be X-ethoxybiphenyl, X-phenylphenol, biphenylene and X-nitrophenol in ratio 7:1.5:1.7:1 respectively. Benzene extract of the crude product was chromatographed (Florisil/Benzene) to give pure 2-phenylphenol (35%) together with<sup>an</sup> unidentified mixture of two materials which<sup>were</sup> thought to be 2-ethoxybiphenyl and biphenylene. No further attempts were made to isolate and identify the other products of this reaction, since the reaction did not look promising as a useful synthesis. The formation of 2-phenylphenol (58) in this reaction is however rather interesting and may involve benzyne as an intermediate. (Scheme 12).

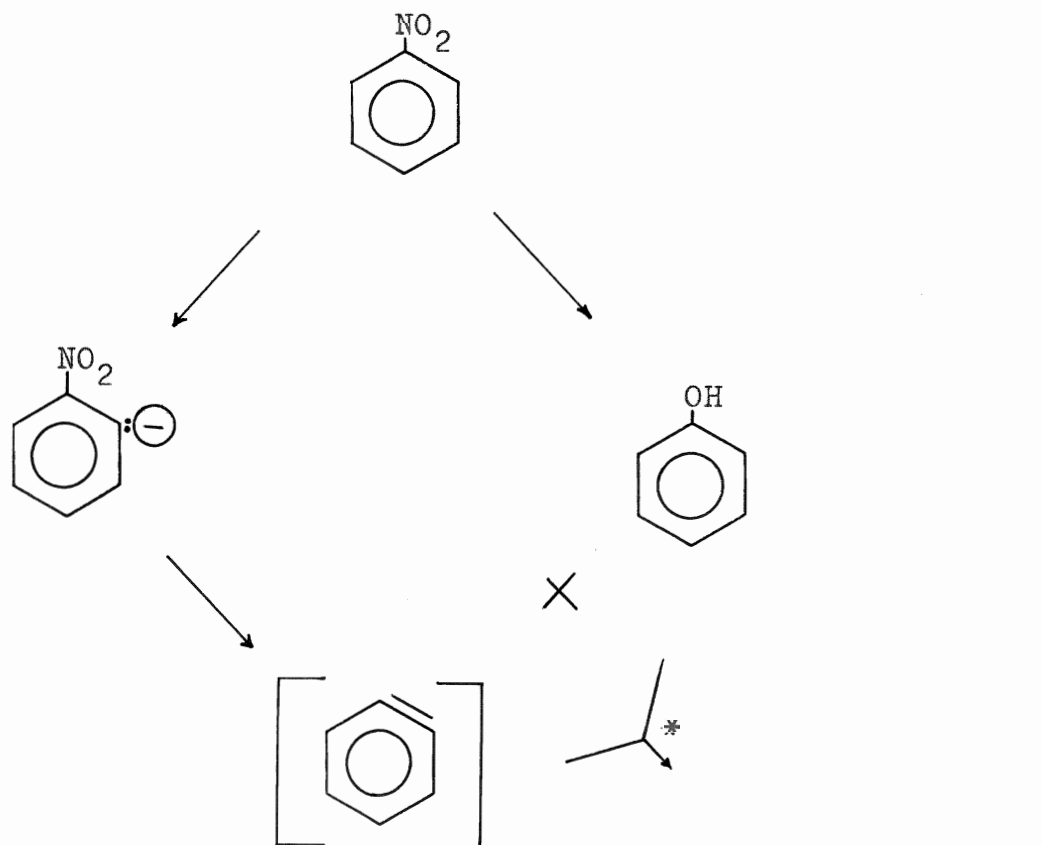


Although the experiment of nitrobenzene is not synthetically useful, it provides probably the first example of aryne formation from an aromatic nitro-compound. One of the main objectives of this work was to study the feasibility of aryne formation from nitro-compounds under these conditions. Unlike the aromatic halogeno-compounds, substitution of a nitro-group into an aromatic system activates the ring to nucleophilic attack at the 2- and/or 4-positions with respect to the nitro-group as well as promoting the acidity of the 2-hydrogens. As a consequence, aryne formation becomes a side reaction instead of being the major one as in the case of halogeno-compounds. In agreement with this, no detectable amounts of aryne-derived products were observed in the case of the more reactive nitro-compounds (e.g., 4-nitrobenzophenone, 44, and 45); instead nucleophilic displacement was favoured.

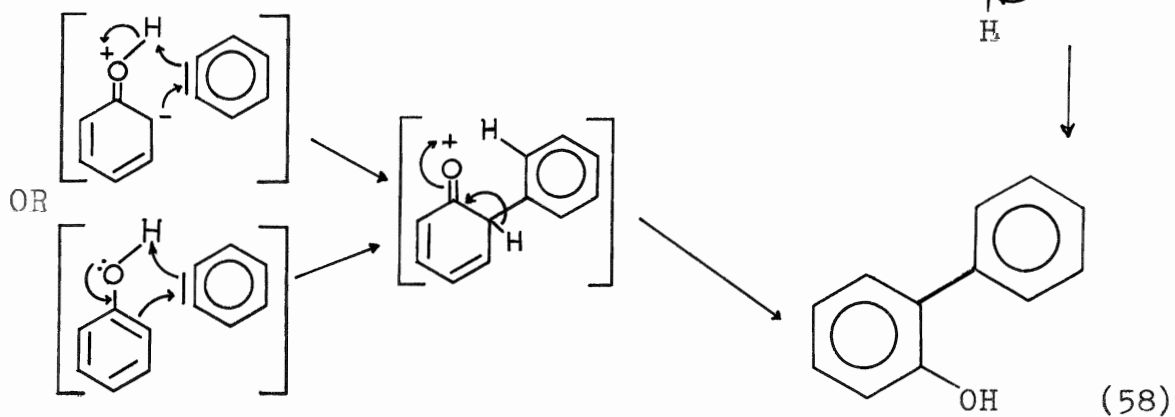
In an aromatic nucleophilic substitution, surprisingly, the nitro-group is a reasonably good leaving group. The most likely explanation is that the first step of an aromatic nucleophilic displacement mechanism (scheme 13) is usually rate-determining, and this step is promoted by groups with a strong -I effect (such as  $\text{NO}_2$ ). This would explain why the nitro-group is such a good leaving group when this mechanism is operating.

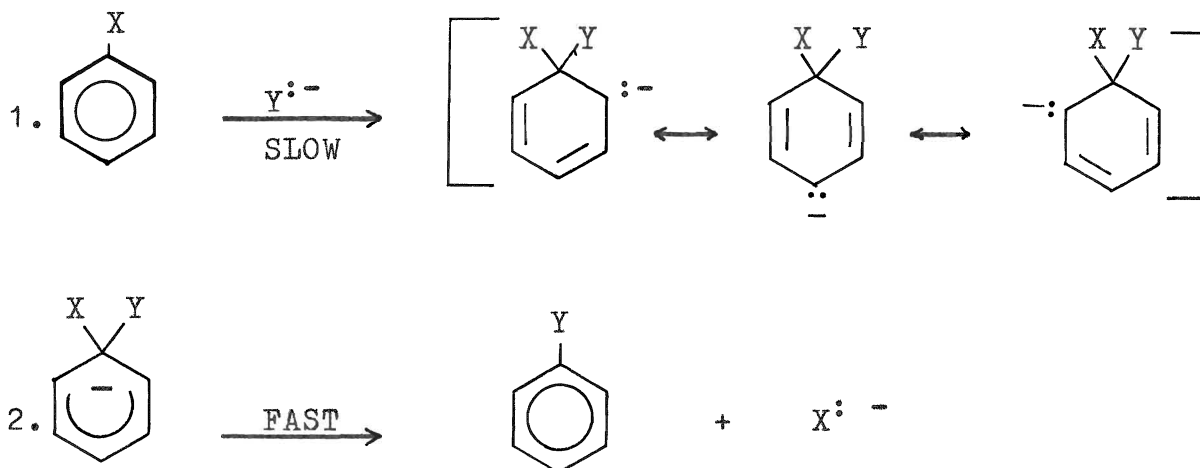
Scheme (12)

POSSIBLE SOURCE OF 2-PHENYLPHENOL

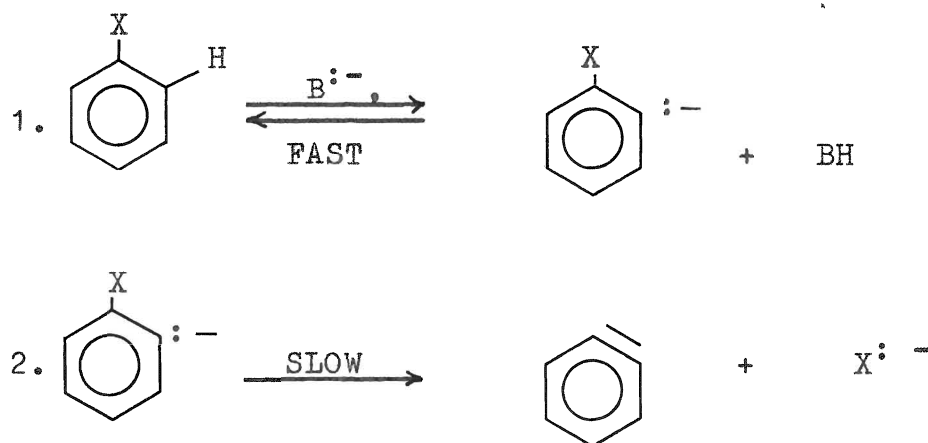


\* Others are possible,  
such as:



Scheme (13)

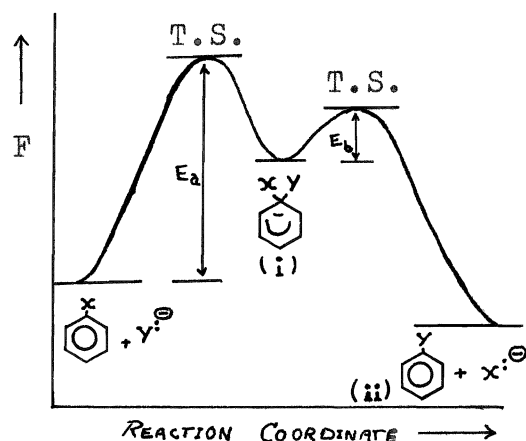
Other considerations are involved when an aryne mechanism is operating (scheme 14). It is most likely that the proton abstraction step (1) will be very much accelerated by the strong  $-I$  effect of the nitro-group. The failure of aryne formation (step 2) is presumably due to the fact that the nitro-group is a poor leaving group under these circumstances.

Scheme (14)

These reactions may also be represented by free-energy diagrams, as illustrated in Figures (I) and (II).

Fig. (I).

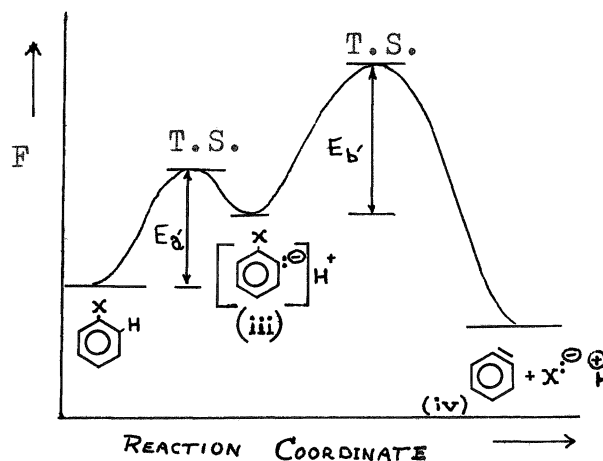
For an aromatic nitro-compound nucleophilic displacement mechanism



Free energy of activation for first stage ( $E_a$ )  $\gg$  free energy of activation for second stage ( $E_b$ ); i.e., first stage is the rate-controlling step of the reaction. That is, the intermediate (i) will pass over to the products (ii) more rapidly than the reactants produce the intermediate.

Fig. (II).

For an aryne-mechanism,  
( $X = -NO_2$ ).

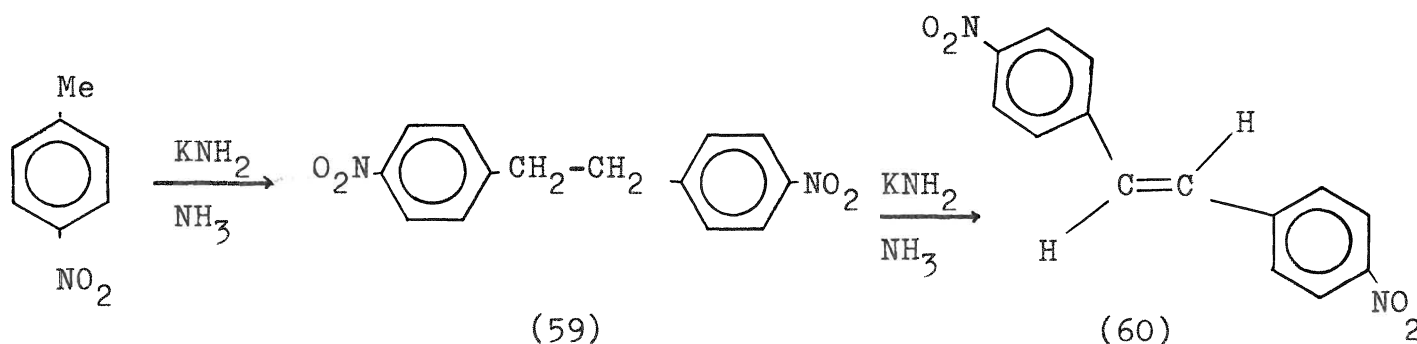


Free energy of activation for first stage ( $E_a'$ )  $<$  free energy of activation for second stage ( $E_b'$ ); i.e., second stage is the rate-controlling step of the reaction. That is, the intermediate (iii) will pass over to the products (iv) more slowly than the reactants produce the intermediate.

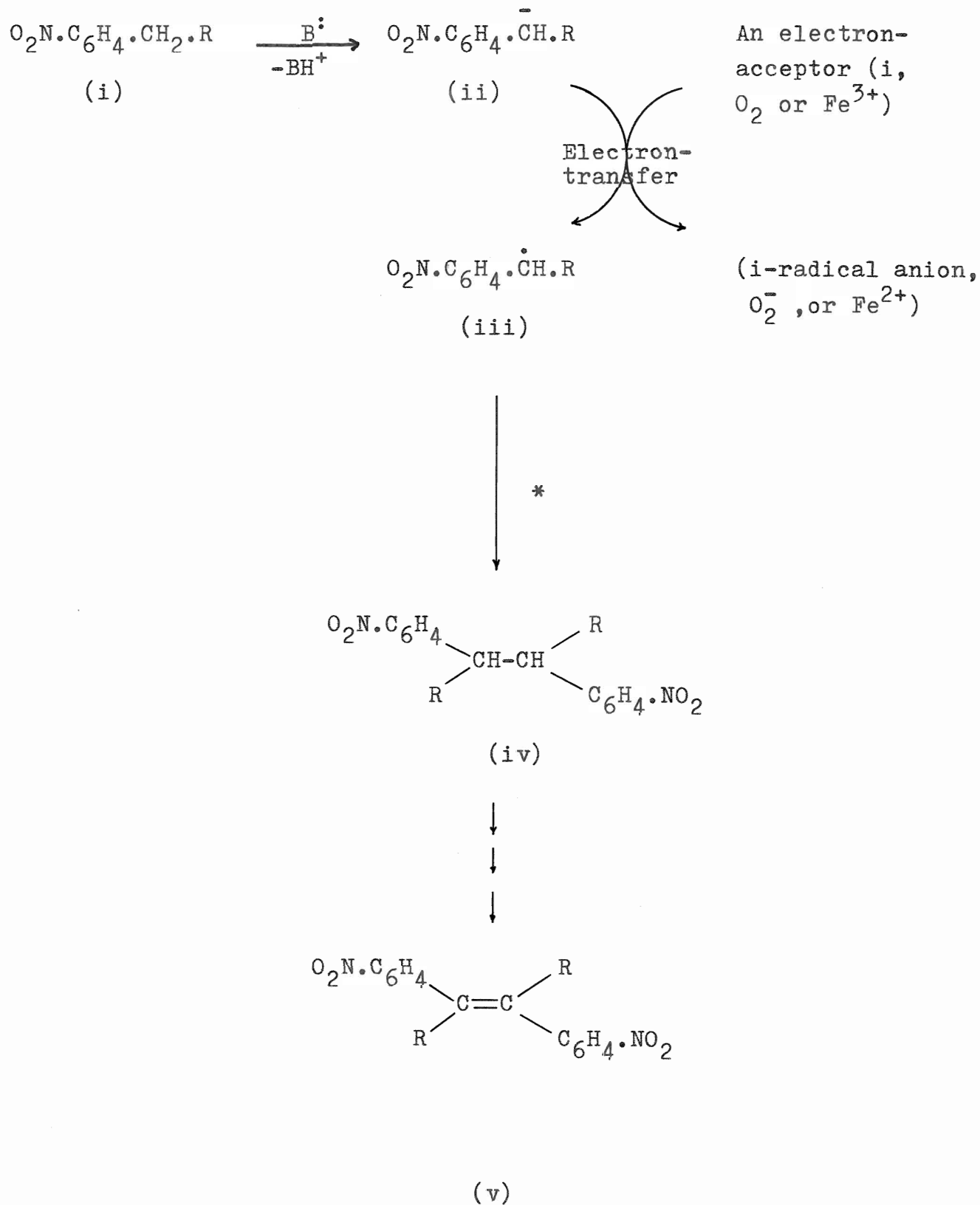
4-NITROTOLUENE

Attention was next directed to the reaction of nitrotoluene derivatives with this reagent. In a preliminary study, Vines<sup>64</sup> had noted that 4-nitrotoluene reacted with potassamide in liquid ammonia to give 4,4'-dinitrobibenzyl (7.3%). This interesting oxidative coupling reaction found by Vines has been observed under other basic conditions, as was mentioned in the Introduction. The Vines' method is of further interest because of the mild conditions employed. It was decided, therefore, to study the feasibility of this coupling reaction with other nitrotoluene derivatives.

Vines' experiment was re-examined under the standard conditions and, surprisingly, found to produce 76.7% of pure 4,4'-dinitrobibenzyl (59). There was also isolated a by-product that was identified as 4,4'-dinitrostilbene (60, 14.8%). It seemed likely that the initial product of the reaction of 4-nitrotoluene with potassamide was the bibenzyl derivative (59) which



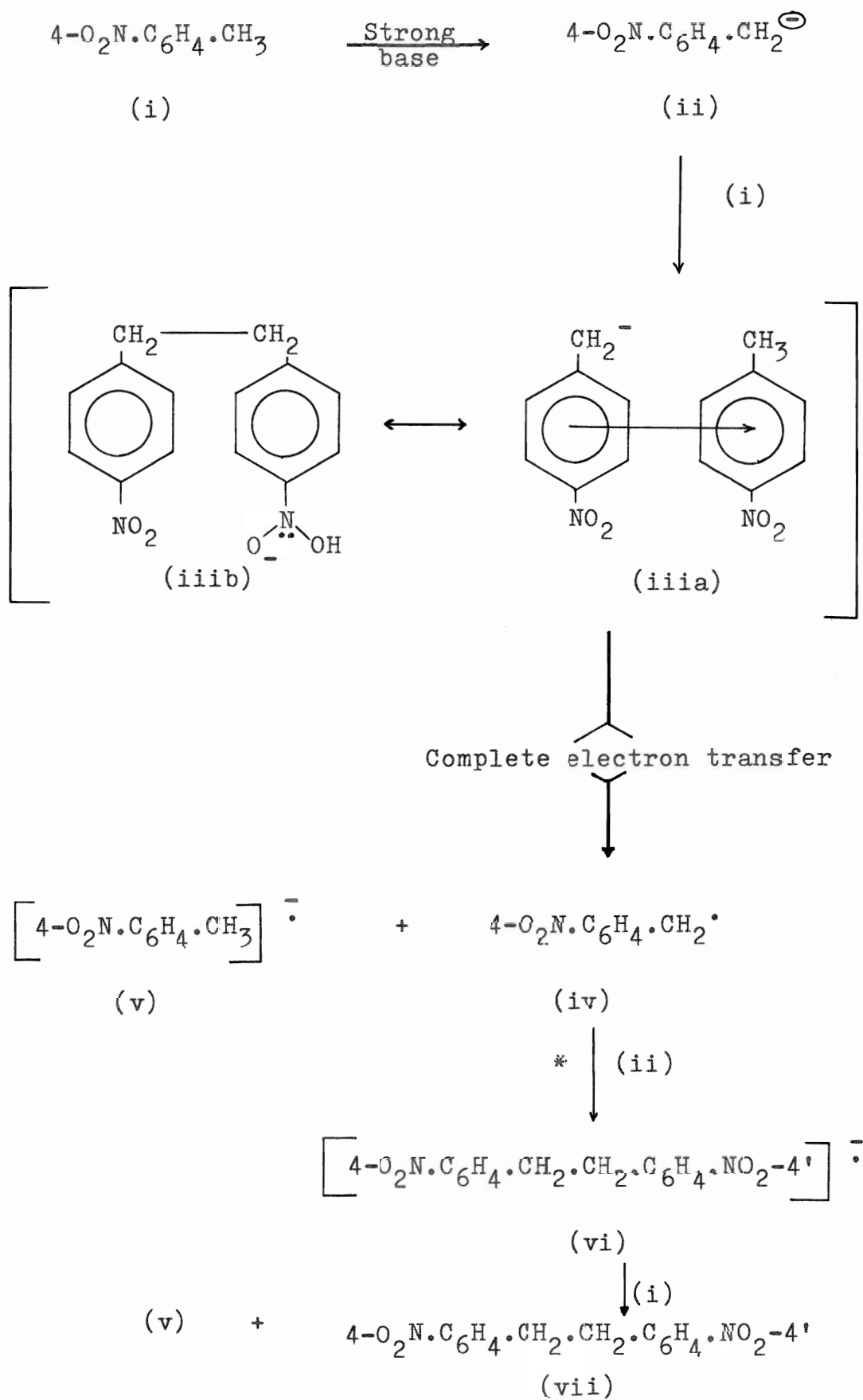
under prolonged reaction conditions was oxidized to give the stilbene derivative (60). 4,4'-Dinitrobibenzyl was therefore treated with potassamide under <sup>the</sup> same conditions and found to give

Scheme (15)

\* See scheme (16).

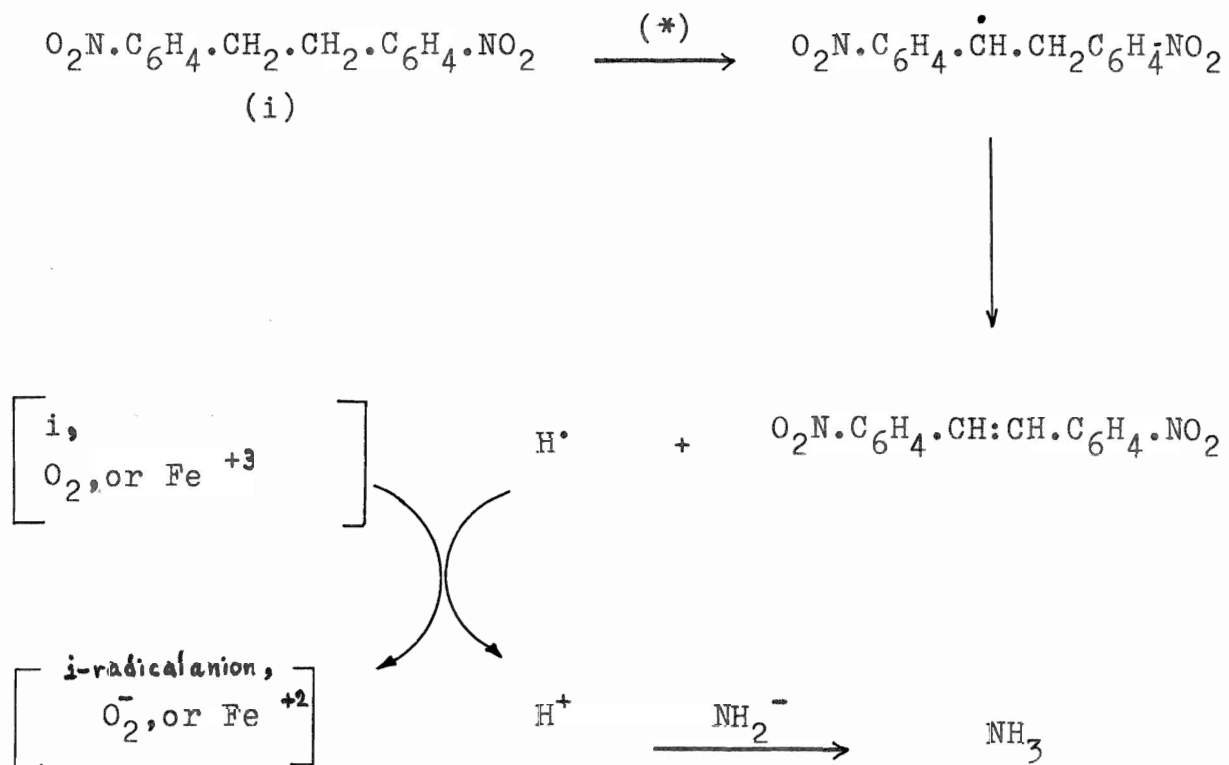


## Scheme (16)



\* Scheme (16) cont., The other possibilities, such as coupling of (a) two radical (iv), (b) radical (iv) with unchanged molecule (i), or (c) radical (iv) with the aci form of (i), have been studied<sup>70</sup> and excluded.

Scheme (17)



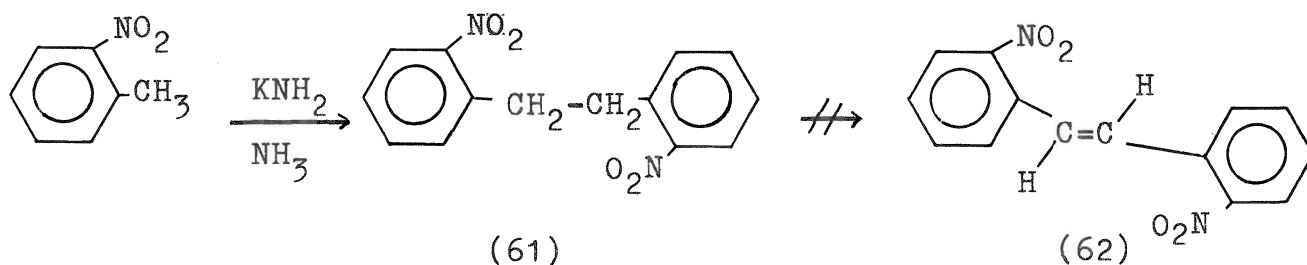
\* See scheme (15).

4,4'-dinitrostilbene ( $\rangle$  72.7%). Moreover, the stilbene derivative (60) is the trans isomer as expected.

It is not clear how the described products are formed, but a simple mechanism similar to that suggested by Davies, Hodge and Yates<sup>17</sup> is possible (scheme 15). This is the simplest reasonable scheme but others are possible<sup>70</sup> (scheme 16). Also it is not clear how the stilbene derivatives described here were formed. Loss of a hydrogen radical may account for the last step (scheme 17), but there is no proof that this mechanism is correct.

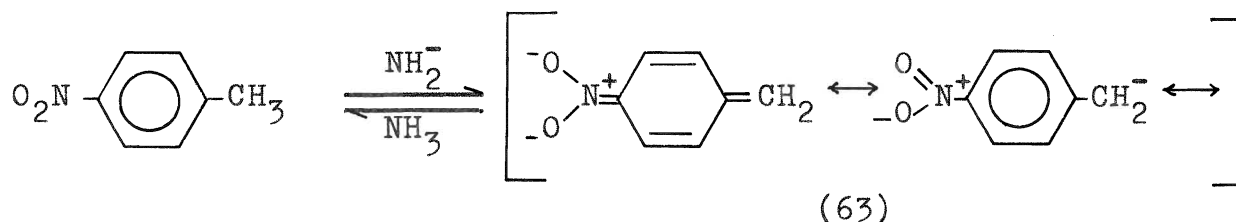
## 2-NITROTOLUENE

2-Nitrotoluene was an interesting molecule for examination under these conditions. In addition to the resonance effect of the nitro-group, the inductive effect of the 2-nitro-group should make the methyl-hydrogens acidic and a coupling reaction might occur easily. 2-Nitrotoluene, when treated with potassamide in liquid ammonia for 4 hours, gave 2,2'-dinitrobibenzyl (61) in 58.5% yield. Longer time of reflux (12 hours) resulted in an increase of yield of (61) to 80.5%, but failed to give any of the stilbene derivative (62). It is not clear why the stilbene derivative (62) did not form upon prolonged treatment. However, it is possible that 2,2'-dinitrobibenzyl did not react further to give the stilbene derivative (62) because of low solubility in the solvent.

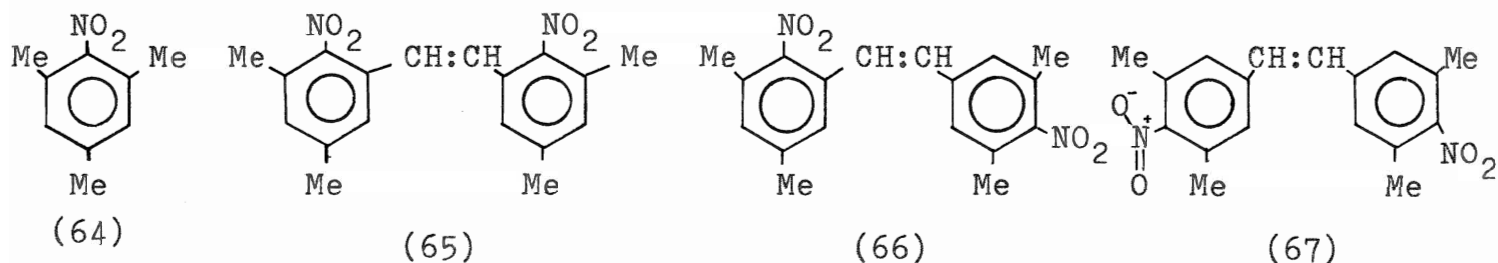


1-NITRO-2,4,6-TRIMETHYLBENZENE

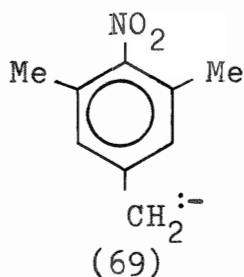
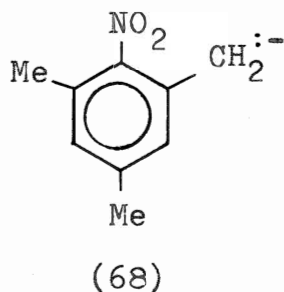
A nitro-group substituted 4- to a methyl-group greatly increases the acidity of the methyl-protons (-R, structure 63). The acidity of these protons should however be lowered by pushing the nitro-group out of the plane of the benzene ring by substitution at 2-positions to the nitro-group. The nitro-group in 1-nitro-2,4,6-trimethylbenzene (64) can exhibit an inductive effect, but the resonance effect is limited. It was, therefore, of interest to examine the behaviour of (64) on treatment with potassamide. It was expected that a coupling reaction of (64) would not be as successful as those occurring in the cases of 2- and 4-nitrotoluenes. 1-Nitro-2,4,6-trimethylbenzene (64) was



treated with potassamide in liquid ammonia for 6 hours. The experiment was worked up in the usual way (see experimental section, p. 96). Surprisingly, a coupling reaction had occurred to give a brown compound of molecular formula  $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4$  in 59 % yield. Three possible structures of the coupled product are (65), (66) and (67):



Since the nitro-group in (64) can only increase the acidity of the methyl-protons inductively, it is most likely that formation of anion (68) is favoured over (69); therefore the structure (65), according to the proposed schemes (15,17), is favoured for the isolated product ( $C_{18}H_{18}N_2O_4$ ).



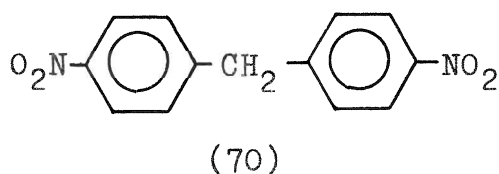
The extreme insolubility of the product made it obvious that a nuclear magnetic resonance spectrum would be extremely difficult to obtain and the true identity of this product remains uncertain.

Mass spectral and elemental analysis are in agreement with formulation as a stilbene derivative such as (65), but not with the bibenzyl derivative that would be involved as an intermediate in the reaction. However, a little piece of evidence was found in the i.r. spectrum; the absorptions at 1600, 1300 and 960  $cm^{-1}$  suggest a trans conjugated  $CH=CH$  group.

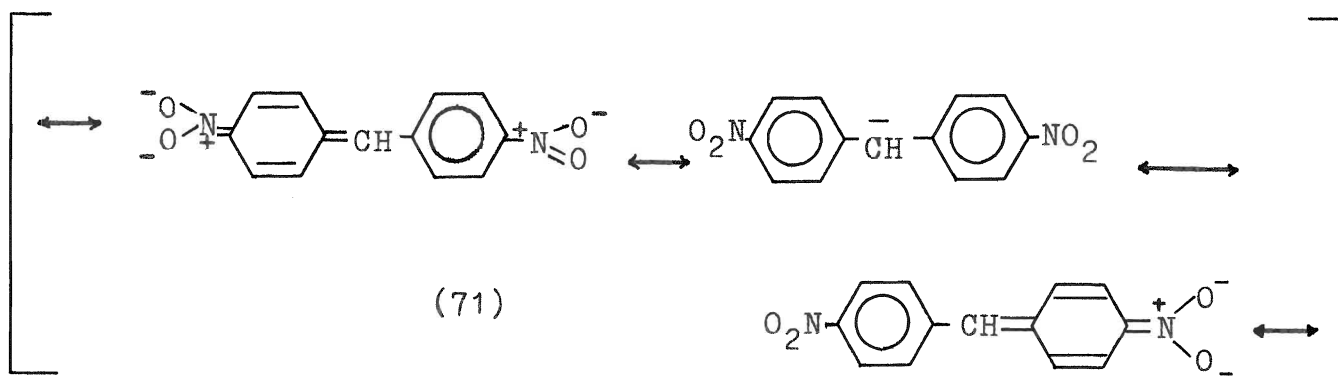
The reaction of alkylaromatic nitro-compounds seems to provide a successful coupling procedure which is synthetically useful. As expected, a nitro-group was found to be essential to provide the necessary activation for a successful coupling reaction; toluene did not react under the same conditions.

#### 4,4'-DINITRODIPHENYLMETHANE

Finally 4,4'-dinitrodiphenylmethane (70) was treated with potassamide in liquid ammonia. Most of the starting material was unchanged.

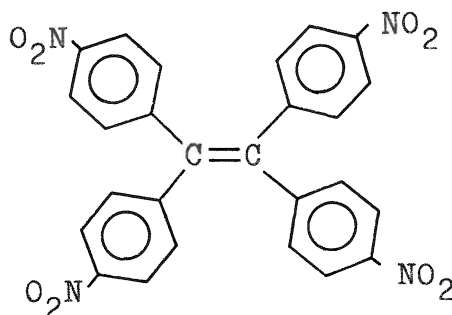


The most likely explanation is that the negative charge on the anion (71) is well delocalised and the anion is relatively unreactive.



The experiment was worked-up as described in the experimental section (p. 98) to give a brown material that was extremely insoluble in most solvents. The extreme insolubility of the product (72) made identification uncertain.

The mass spectrum of the product showed molecular ion at  $m/e$  512 a.m.u. and fragmentation peaks in agreement with the proposed structure (72).



(72)

Furthermore, a solid-phase infrared spectrum confirmed the stilbene structure ( characteristic absorption at  $1625-1675\text{ cm}^{-1}$  indicated  $\text{C}=\text{C}$  ).

#### CONCLUSIONS:

It seems that aromatic nitro-compounds react with amide ion at low temperatures in many ways to give products that vary considerably with the reactant. Similar behaviour has been found with many other bases.

A variety of bibenzyl, and stilbene derivatives can now be synthesised in good yields using this new reagent and mild conditions.

3-Amino-4-nitrobenzophenone can be prepared using this method; this is valuable since no alternative approach to this compound is indicated in the literature.

A useful feature of using this medium is that other nucl-

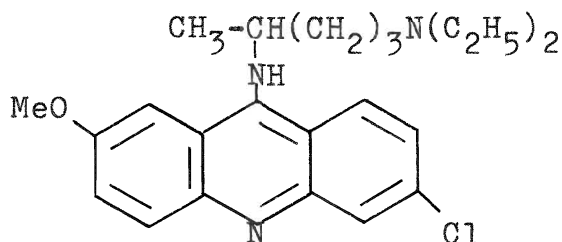
eophiles (such as  $\text{RO}^-$ ) can be used as competitors with amide ion under these mild conditions of low temperature. For example, the reaction of 4-nitrodiphenyl sulfone (44) in ethanol with this reagent gave 4-ethoxydiphenyl sulfone (52, 65%) and 4-ethoxynitrobenzene (53, 29%).



## SECTION (II)

### THE TREATMENT OF SELECTED ANTHRAQUINONES AND RELATED COMPOUNDS WITH FORMAMIDE AND N-METHYLFORMAMIDE

Acridine derivatives have been of interest for a considerable period of time. For example, 2-methoxy-6-chloro-9-(4'-diethylamino-1'-methylbutyl)-aminoacridine (73), also called quinacrine<sup>71</sup>, mepacrine, or atebrin, is a valuable antimalarial drug. Other acridines have attracted attention as medicinals, e.g., acriflavine (3,6-diamino-10-methylacridinium chloride) against sleeping sickness and as an anti-bacterial agent, and Rivanol (3,9-diamino-7-ethoxyacridine) against amoebic dysentery.



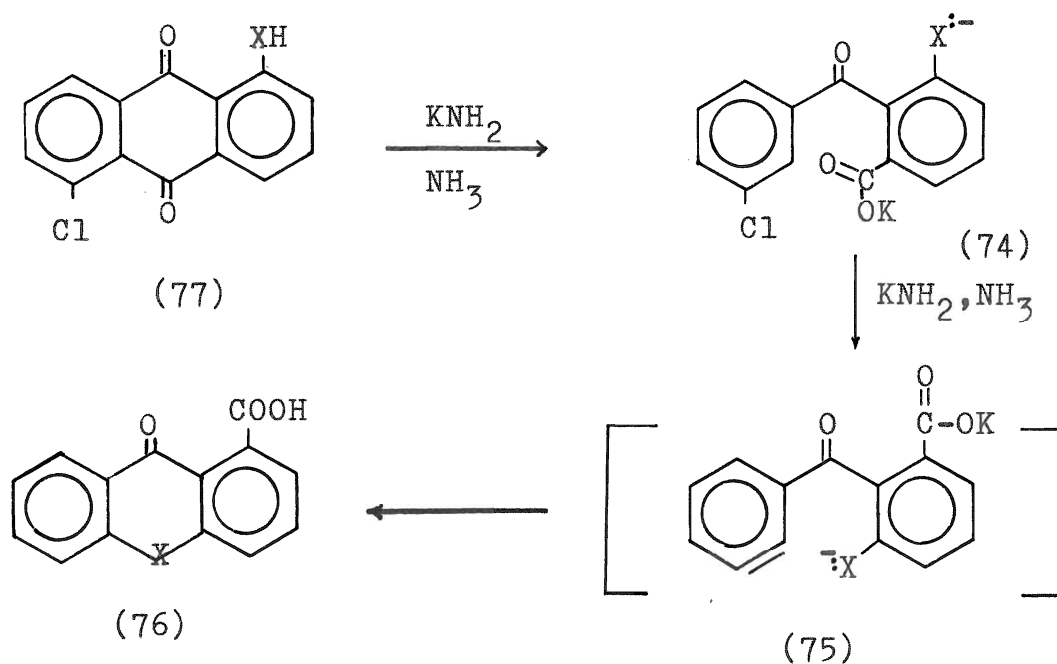
(73)

Again, there is considerable interest in the synthesis of acridone derivatives. Very recently, a number of acridone carboxylic derivatives have been reported<sup>72</sup> as anti-allergic agent. The present work reports the preparation of the first example of an acridone-1-carboxylic acid derivative.

A new acridone synthesis might well be useful, since only two general methods are available for the synthesis of these compounds, one involving high temperature nucleophilic substitution and the other involving high temperature treatment with acid.

The work of Chen<sup>35</sup> (cf. page, 20) showed that 1-chloro-anthraquinone does not undergo cleavage at either carbonyl group to any significant extent when treated with potassamide in liquid ammonia. Instead, 1-amino- and 2-aminoanthraquinones were obtained. Under these conditions, Kayser and Gibson<sup>73</sup> were able to show that 1,5-dichloroanthraquinone was cleaved to give 3-chlorobenzoic acid only.

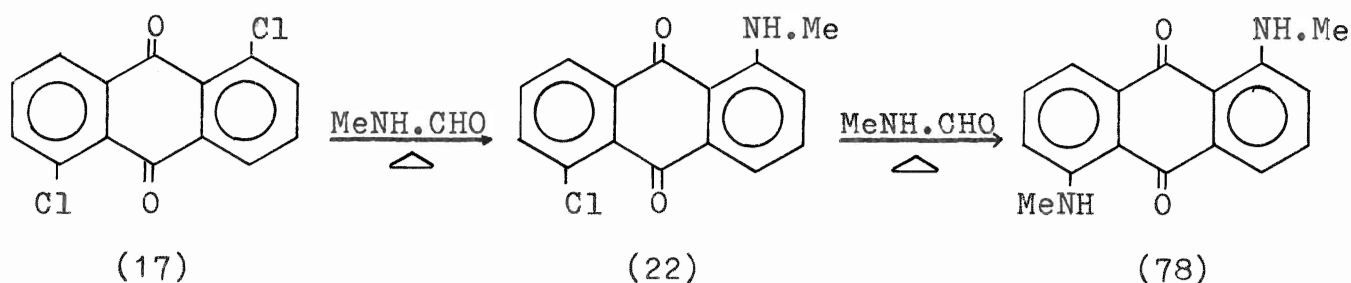
It was thought that, by replacing one of the chlorine atoms in 1,5-dichloroanthraquinone with another group-X (such as,  $\text{RN}^-$ ,  $-\text{O}^-$ , or  $-\text{S}^-$ ) which is comparatively less electron withdrawing than chlorine, cleavage at the carbonyl group adjacent to chlorine might be achieved to give the benzophenone derivative (74). An aryne intermediate such as (75) should then be generated under these conditions. The nucleophilic centre  $\text{X}^-$  could then add intramolecularly to the aryne, and finally a proton would be acquired to give (76).



Attempts were made by this writer to synthesise the required starting material (77). As was mentioned in the Introduction, two methods for preparation of 5-chloro-1-N-methylaminoanthraquinone have appeared in the literature. Hall and Hey<sup>31</sup> showed that a mixture of 1,5-dichloroanthraquinone (17) and pyridine containing methylamine upon heating in a pressure bottle afforded dark red material which gave, after sublimation and crystallisation from glacial acetic acid, 5-chloro-1-N-methylaminoanthraquinone. Lord and Peters<sup>32</sup> were able to isolate 5-chloro-1-N-methylaminoanthraquinone (2.4%) from a mixture of three components produced by refluxing 1,5-dichloroanthraquinone (17) with dimethylformamide for 21 hours.

However, these two literature methods suffer from the disadvantage of being unsuitable in terms of purity or of yield for further experimentation. In Hall and Hey's method, extensive purification steps were used; no spectroscopic evidence was presented to confirm the purity, and no % yield was given. Further, the low yield (2.4%) in Lord and Peters' method and the absence of elemental analysis and spectral data raised doubts about its usefulness.

For these reasons, it was decided to approach the synthesis of (22) from (17) using N-methylformamide as reagent. Reasonable yields (35-43%; almost theoretical yield based on the recovered starting material) were achieved and compound (22) was obtained pure for the first time. However, a prolonged reaction time resulted in the formation of 1,5-bis-(N-methylamino)-anthraquinone (78).



Chromatography separated mixtures of (22) and (78) from unchanged starting material, but did not separate (22) and (78) from each other as their  $R_f$  values were too similar. For this reason, it was decided to stop the reaction before (78) was formed in detectable amounts. The refluxing mixture of (17) and N-methylformamide was monitored by obtaining the mass spectrum, since t.l.c. (Benzene or Chloroform/Silica gel) did not separate a mixture of (22) and (78). The results are summarised in Table (I).

Mixtures of (17) and (22) were successfully separated by chromatography on Florisil using benzene or benzene-ligroin (1:1) mixture as eluants. Further crystallization from chloroform afforded essentially pure (22). Most of the unchanged starting material was easily recovered and crystallized from benzene for reuse.

Without further experimentation it is not clear how the reaction proceeds. However, the deformylation step is believed to occur after initial nucleophilic attack at the carbon atom bearing the chlorine.

TABLE (I): THE REACTION OF 1,5-DICHLOROANTHRAQUINONE  
WITH N-METHYLFORMAMIDE.

No.	# of grams of (17)	N-Methyl- formamide (ml.)	Reflux (hrs.)	%		
				m/e 276	m/e 271	m/e 266
1.	3.4	10	60	NONE	38	100
2.	3.4	15	24	NONE	35	100
3.	3.4	20	24	TRACE	4.2	100
4.	3.4	20	14	TRACE	35	100
5.	3.4	20	11	33	100	25.4
6.	3.4	20	10	48.4	100	22.5
7.	3.4	20	8	63.6	100	18.2
8.	3.4	20	6	98	100	10.5
9.*	3.4	20	3	100	50	TRACE
10.**	3.4	30	24	TRACE	TRACE	100

\* Experiment #9 was used for preparation of (22).

\*\* Experiment #10 was used for preparation of (78).

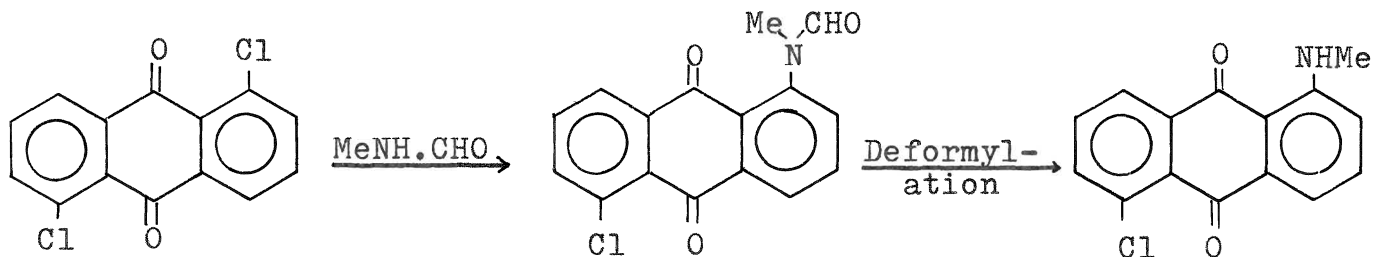
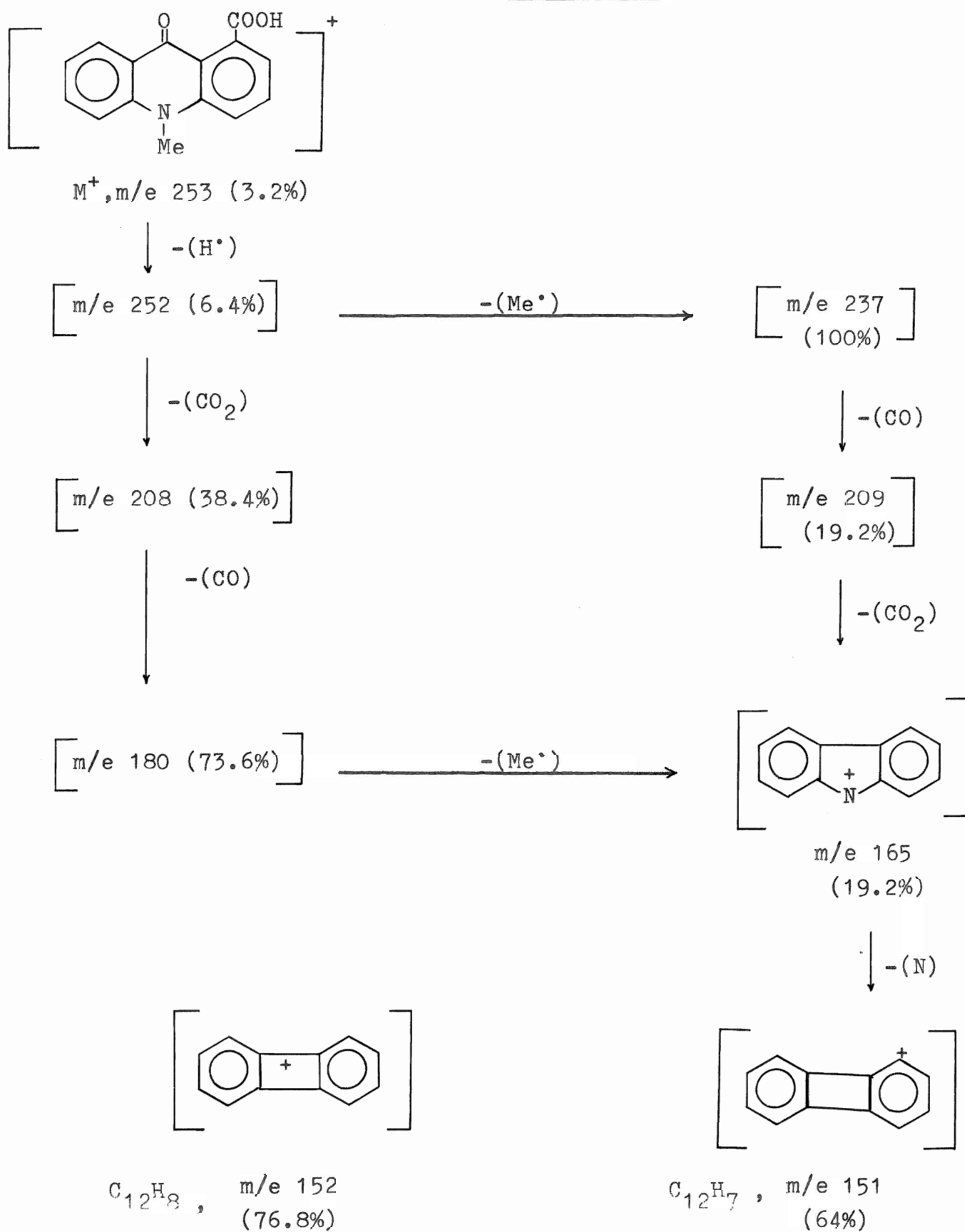
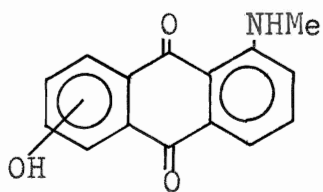


TABLE (II)

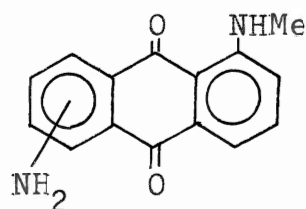


5-Chloro-1-N-methylaminoanthraquinone was treated with potassamide in liquid ammonia for 4 hours. An ether extraction process of the basic fraction (see experimental section, cf. page 102) afforded a red material (65%) which was shown to be a new compound contaminated with a little unchanged starting material.

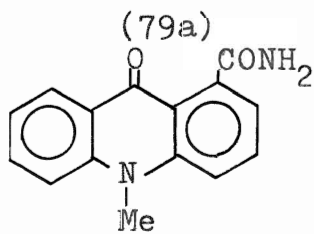
Chromatography separated an unidentified yellow material and unchanged starting material from the desired product which was finally obtained as red needles (47% yield). Mass spectral analysis (Table II) permitted rejection of structures (79a), (79b) and (79c) and suggested structure (79d), N-methylacridone-1-carboxylic acid.



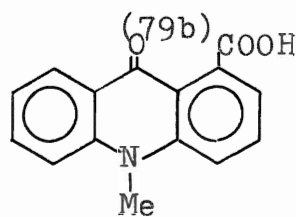
(79a)



(79b)



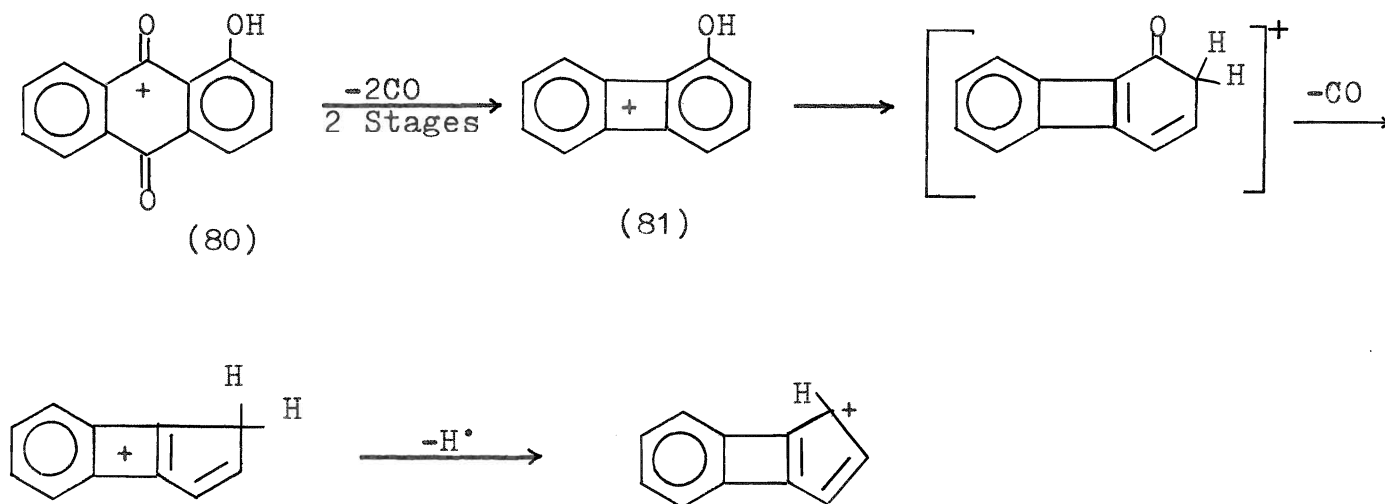
(79c)



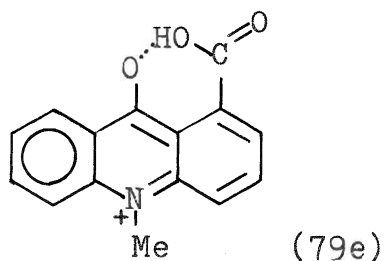
(79d)

Quinones and, in particular, 9,10-anthraquinones show a very characteristic fragmentation behaviour in mass spectrometry. Aside from an intense molecular ion peak, the most characteristic feature is the occurrence of ions corresponding to the loss of one and of two molecules of carbon monoxide. In hydroxyanthraquinones (e.g., 80), the successive expulsion of two molecules of

carbon monoxide leads to a hydroxybiphenylene ion (81), which exhibits further loss of carbon monoxide as well as of CHO.



On these bases, the mass spectrum of the red product permitted rejection of structure (79a). In addition to mass spectral evidence, elemental analysis allowed exclusion of structures (79b) and (79c), since only one nitrogen atom is present. The compound



has a red colour possibly because of the strong hydrogen-bonding (79e); recent work<sup>59</sup> has shown the relationship between the hydrogen-bonding and colour. However, the i.r. spectrum does not pro-



vide confirmatory evidence of hydrogen-bonding ; thus the C=O stretching vibrations of both carbonyl groups were not shifted to lower wavenumbers. Further evidence supporting structure (79d) was found in the i.r. spectrum:

(1) Absorption peaks at  $1730$  and  $1200\text{ cm}^{-1}$  corresponding to  $\beta$ -haloketo group in the spectrum of the starting material (22) are not apparent in the spectrum of the product (79). This, however, does not exclude structures (79a), (79b) and (79c).

(2) A new absorption peak occurring at  $3280\text{ cm}^{-1}$  may correspond to a carboxyl group (79d) or H-bonded phenolic group (possibly 79e), but not to a free phenolic group or  $\alpha$ -hydroxy aromatic carbonyl grouping which usually appears at higher wavenumbers ( $>3500\text{ cm}^{-1}$ ).

The  $^1\text{H}$ -n.m.r. spectrum of the starting material (22) shows a doublet (3H) at  $\delta\ 3.0$  corresponding to the methyl group. By contrast, the spectrum of (79) shows a singlet (3H) indicating that the coupling between the methyl-protons and -NH- proton is no longer present. Moreover, a broad absorption at  $\delta 10.0$  ( $-\text{COOH}$ ) is observed, while a singlet (1H) at  $\delta\ 1.3$  ( $-\text{NH}-$ ), detectable in (22), is absent from the spectrum of the product (79).

It seemed that treatment of 5-chloro-1-N-methylaminoanthraquinone with other bases than amide would provide additional proof. If reaction were to occur, the product would not be (79b) or (79c). Potassium t-butoxide was used and tert-butylbenzene was found to be a suitable solvent; reaction occurred and gave the same product (79d) as that obtained from the reaction of (22) with potassamide.

The successful synthesis of (79d) led to attempts to synthesise the required starting materials for similar preparations of 1-carboxylic derivatives of acridone, xanthone and thioxanthone.

In an attempt to synthesise the next intermediate (77, X = -NH-), 1,5-dichloroanthraquinone was treated with 4-toluenesulfonamide, anhydrous potassium carbonate, copper acetate and nitrobenzene for 4 hours according to a literature method<sup>31</sup>. Although traces of 1-(4-toluenesulfonamido)-5-chloroanthraquinone were formed ( $M^+$ , 411; m.p. 196°), the reaction failed to provide enough material for further experimentation and most of the starting material was unchanged.

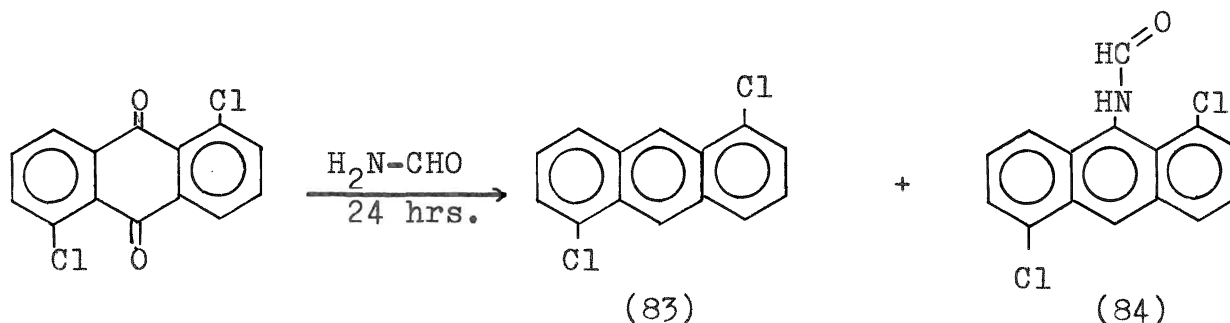
In another attempt, 1,5-dichloroanthraquinone was treated with formamide in the hope of introducing an amino-group via a chlorine displacement analogous to that which occurred with N-methylformamide. However, none of the desired product was isolated. Instead, a rather interesting result was obtained. The reagent reacted with the carbonyl groups in a novel way, reminiscent in some respects of the Leuckart reaction, to give unexpected anthracene derivatives. This interesting result drove this writer to look further at applying the Leuckart process to anthraquinones. This part of the work is discussed separately in the next pages.

In an attempt to synthesise the intermediate (77, X = -S-), 1,5-dichloroanthraquinone was treated with sodium sulfhydrylate in benzyl alcohol for 9 hours. However, none of the desired product was isolated. Instead, di(5-chloroanthraquinon-1-yl)-sulfide was obtained (see the Experimental section, p. 105).

THE ANTHRAQUINONES AND THEIR UNUSUAL REACTION  
WITH FORMAMIDE

As was mentioned above, this part of the research was developed as a result of trying to extend a new acridone synthesis to the case of  $X = \text{NH}$  by use of formamide. Although it was known from Schiedt's work<sup>56</sup> (discussed later) that anthraquinone reacts with formamide to give 9,10-N,N'-diformylaminoanthracene (82), it was hoped that 1,5-dichloroanthraquinone would undergo, instead, chlorine displacement under these conditions, a reaction type that was demonstrated with N-methylformamide and used to introduce the N-methylamino-group in place of chlorine.

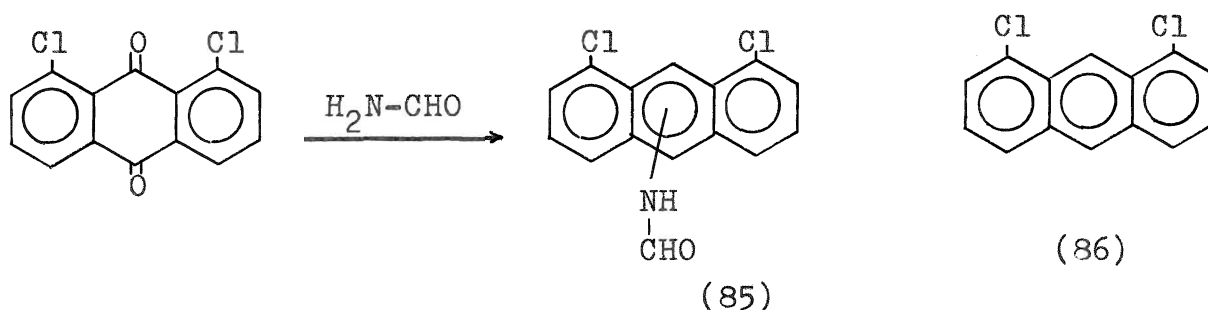
Treatment of 1,5-dichloroanthraquinone with excess of formamide for 24 hours gave 1,5-dichloroanthracene (83, 26.5%) and its 9-N-formylamino-derivative (84) in 5.6% yield.



It was clear that 1,5-dichloroanthracene resulted from further reaction of the 9-N-formylamino-compound (84) with formamide (or a derivative thereof), since a shorter time of reflux resulted in a lower yield of (83) (19.8%), while the yield of (84) increased to 26.6%. In view of the experiments just described however, it was desirable to ascertain whether the additional activation resulting from the presence of chlorine atoms in the anthraquinone system was in fact necessary, since it was known

from Schiedt's work that treatment of anthraquinone with formamide for 4 hours gave N,N'-diformyl-9,10-diaminoanthraquinone only.

It could be expected that the prolonged reaction of formamide with anthraquinone derivatives such as 1,8-dichloro-, 1-chloro-, and possibly 2-chloroanthraquinone and anthraquinone itself would form the corresponding anthracenes. When 1,8-dichloroanthraquinone was refluxed in formamide (results are summarised in table III) for three hours, only 1,8-dichloro-X-N-formylaminoanthracene (85) was isolated in 95.7% yield. After 6 hours reflux, however, a new compound was produced which was separated on silica gel (thin layer) and shown to have a molecular ion of  $m/e$  246 and reasonable fragmentation in agreement with the expected compound, 1,8-dichloroanthracene (86). Attempts to isolate (86) were made.



1,8-Dichloro-X-N-formylaminoanthracene was refluxed with formamide for 16 hours. A benzene extract was chromatographed to give pure (86) in 14% yield; unchanged (85) was easily recovered (90%).

At this stage, the method looked promising as a general route to anthracenes, at least from the activated anthraquinones.

TABLE (III): REACTION OF 1,8-DICHLOROANTHRAQUINONE  
WITH FORMAMIDE.

STARTING MATERIAL	REFLUX TIME (hrs.)	STARTING MATERIAL RECOVERED %	PRODUCT(S)	%YIELD (based on theoretical yield)	%YIELD (based on % of starting M. recovered)
1,8-di-chloro-anthra-quinone	3	NONE	(85)	95.7	95.7
"	6	NONE	(85)+(86)	76.3	76.3
(85)	16	85	(86)	13.6	89.5

Three main features of this method are:

- (1) A variety of anthraquinones are available.
- (2) High yields, based on recoverable starting material, are obtained.
- (3) It can be an ideal method for commercial use, since the conditions required are:
  - a. Simple reflux in formamide; excess of formamide can be recovered by distillation.
  - b. Solvent extraction (usually benzene), followed by chromatography, gives the pure product and the solvent can be recovered.
  - c. Finally, there are few side reactions, and unchanged

starting materials can be easily recovered.

Examining the reactions of other anthraquinones seemed to be necessary. Table (IV) summarises the results of the reactions of 1-chloro- and 2-chloroanthraquinones. It thus appeared

TABLE (IV)					
STARTING MATERIAL REFLUXED WITH FORMAMIDE	REFLUX TIME (hrs.)	% OF STARTING MATERIAL RECOVERED	PRODUCT(S)	% YIELD (based on theoretical yield)	% YIELD (based on % Of starting material recovered)
1-Chloro-anthraquinone	8	NONE	1-Chloro-X-N-formyl aminoanthracene (87)	94	94
(87)	16	81 <sup>*</sup>	1-Chloro-anthrane (88).	8.6	48
2-Chloro-anthraquinone	8	NONE	2-Chloro-9,10-N,N'-diformyl-aminoanthracene (89)	92	92
(89)	16	98 <sup>**</sup>			
<p>* Contaminated with some of (88).</p> <p>** Contaminated with trace of two new compounds.</p>					

that the reductive displacement of the formylamino-group under the conditions employed was more difficult in cases where there was no electron-withdrawing group (such as chlorine) adjacent to

the reaction site. Furthermore, the more strongly activated the anthraquinone, the more easily would reductive displacement take place; this was demonstrated by the higher yield of the corresponding anthracenes obtained in the series 1,5-dichloro- $\rangle$  1,8-dichloro- $\rangle$  1-chloro- $\rangle$  2-chloroanthraquinones.

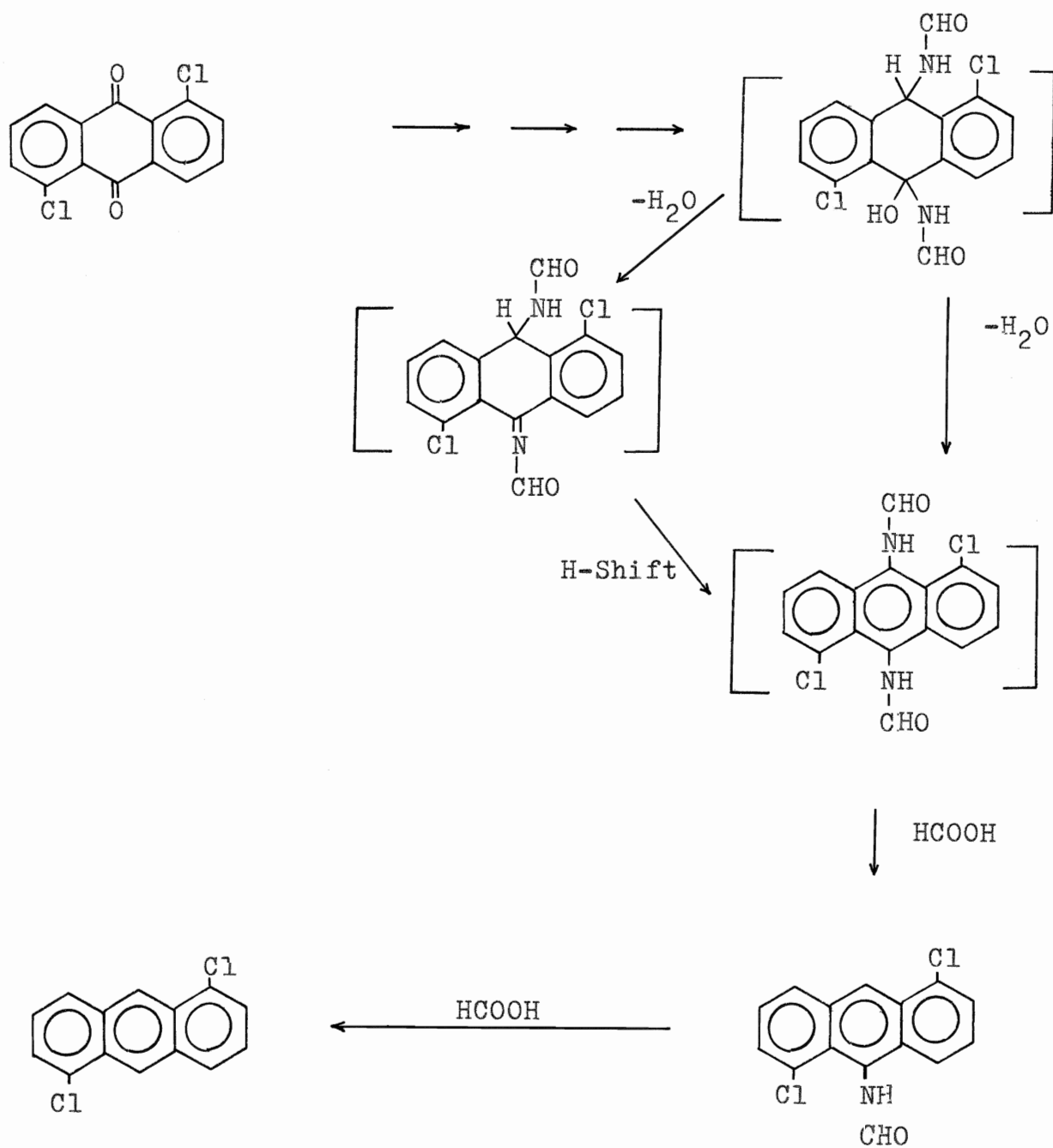
The formation of the anthracenes from the corresponding anthraquinones has now been shown to be a general occurrence, and it can be enhanced in the case of the less reactive compounds by modifying the required conditions, e.g., by using a suitable catalyst or longer time of reflux.

In examples studied so far, reductive displacement or reduction have been supposed to involve formic acid. It was therefore desirable to ascertain whether formic acid, assumed to be released on heating formamide at 165-200<sup>0</sup>, was in fact necessary. Treatment with formic acid would fulfil a number of purposes. If addition of formic acid accelerated the reaction, evidence of its involvement in the reaction with formamide would be apparent. If the yield increased significantly, this would provide the first step in the modification of this procedure.

1,8-Dichloro-X-N-formylaminoanthracene (85), 1-chloro-X-N-formylaminoanthracene (87), and 2-chloro-9,10-N,N'-diformylaminoanthracene (89) were, therefore, subjected to this treatment. The results are summarised in table (V).

The reaction mechanism can be explained reasonably in terms of the intermediate (90) obtained as a result of steps in a Leuckart-type reaction (discussed in the Introduction); instead of producing the expected Leuckart product (91), loss of a molec-

Scheme (13)\*

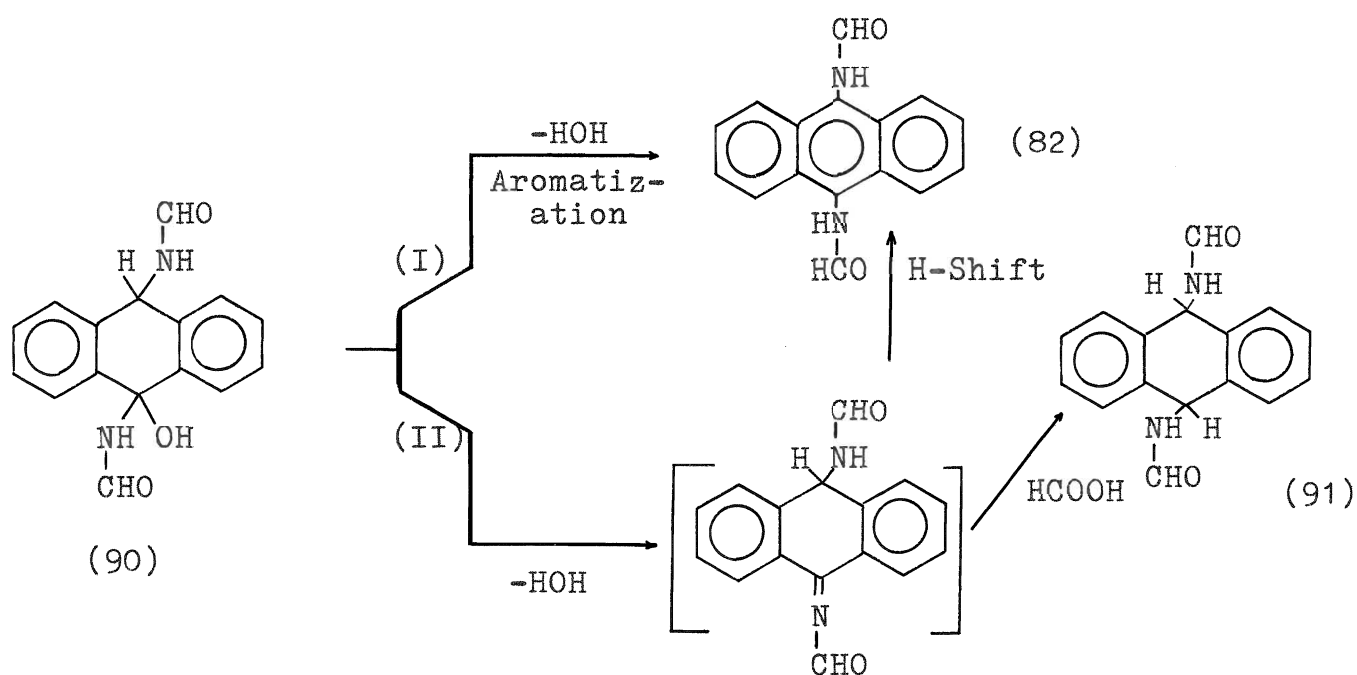


\* One quinone, 1,5-dichloroanthraquinone, only is shown.



TABLE (V) : REACTIONS OF N-FORMYLAMINOANTHRACENES WITH FORMIC ACID IN FORMAMIDE.					
STARTING MATERIAL	REFLUX TIME (hrs.)	% OF S.M. RECOVERED.	PRODUCT(S)	% YIELD (based on theoretical yield)	% YIELD (based on % of S.M. recovered)
(85)	48	80	(86)	18.1	90.6
(87)	9	73*	(88)	19.5	72.2
(89)	9	94.3**	—	—	—
* Contaminated with some of (88). **Contaminated with trace of two new compounds.					

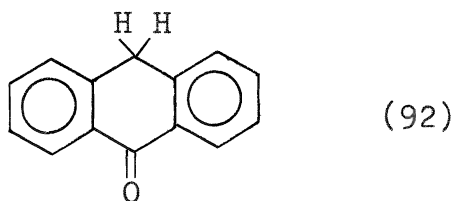
ule of water from (90) by route (I) or (II) then gives the diformylamino-derivative (82). The proposed reaction sequence is shown in scheme (18). This mechanism is based on the different



products which have been obtained from various starting materials and discussed in this thesis. These data suggested the following sequence: (Anthraquinone derivative)  $\xrightarrow{1.}$  (Di-formylaminoanthracene derivative)  $\xrightarrow{2.}$  (Mono-formylaminoanthracene derivative)  $\xrightarrow{3.}$  (Anthracene derivative).

The least reactive anthraquinones (e.g., anthraquinone and 2-chloroanthraquinone) have been shown to give the first step products which reacted very slowly to give the products of steps 2 and 3. The more reactive anthraquinones (e.g., 1,5-, and 1,8-dichloro- and 1-chloroanthraquinone) have been shown to react very quickly to give directly the corresponding products of step 2 in high yields; after prolonged reaction, these give the products of step 3, the anthracene derivatives.

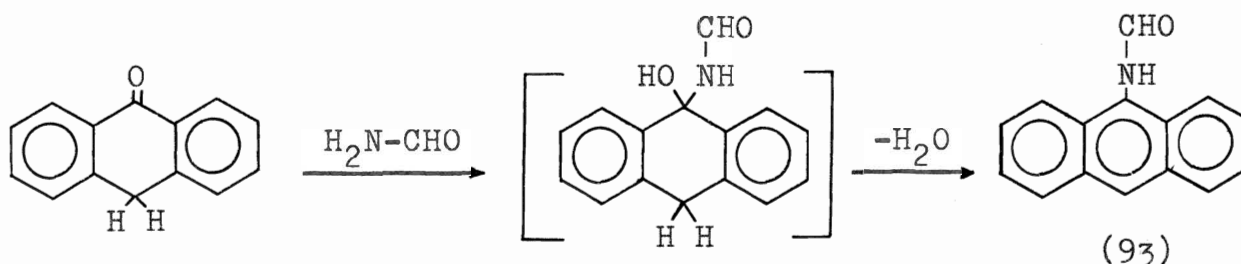
The reductive displacement of the formylamino group is believed to be effected by the action of formic acid liberated from formamide (equation 9, page 22). Intermediates such as (91) or (92) are not acceptable for the following reasons:



(a) Intermediate (91) has to lose 2H in order to give the obtained product. This is not a favoured process under such reductive conditions.

(b) The reaction of anthrone (92) has been studied by this writer and shown to proceed in different way, as mentioned

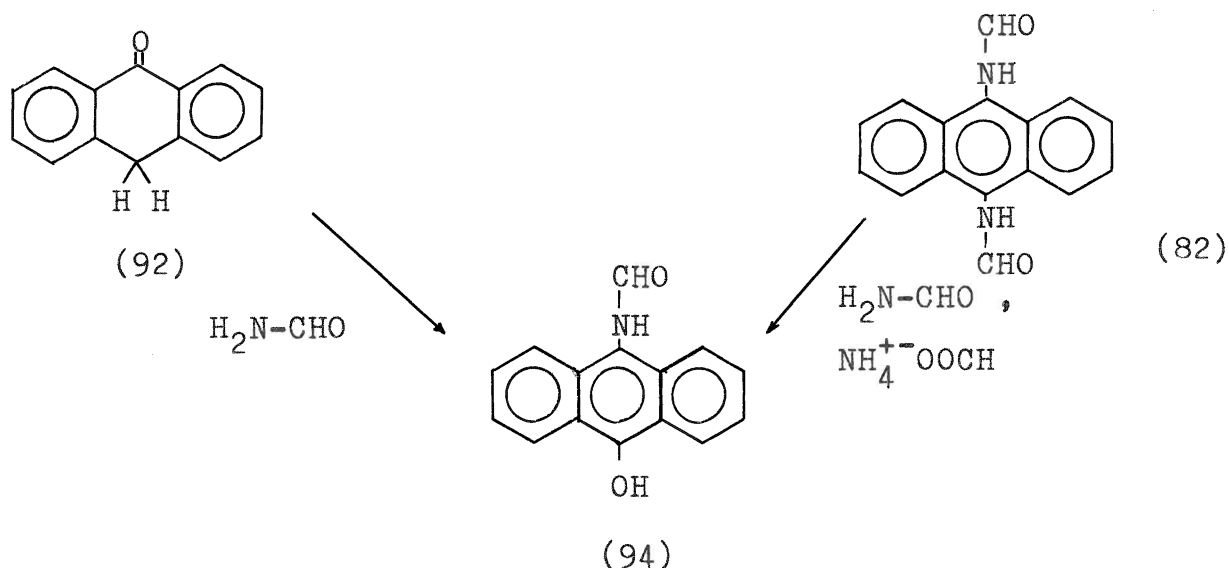
later. It was in any case likely that anthrone, if involved, would give the mono-formylamino derivative (93) instead of the diformylamino derivative (82).



It is most likely that the mono-formylamino derivatives obtained from the reaction with 1,8-dichloro- and 1-chloroanthraquinones are 1,8-dichloro-10-N-formylamino- and 1-chloro-10-N-formylaminoanthracenes respectively, since it was shown that displacement of formylamino-group proximate to the electron-withdrawing chlorine atom is much easier than one further removed from the chlorine atom. However, attempts were made to solve this orientation problem. Addition of shift reagents, it was hoped, would provide more resolution to the  $^1\text{H.n.m.r.}$  aromatic protons pattern. Eu-resolve,  $\text{Eu}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$ , was added in successive portions to an n.m.r. sample of (85) dissolved in  $\text{d}_6\text{-DMSO}$ . Better resolution did not occur; instead the aromatic protons pattern became broad, the broadness of the pattern increasing when the amount of the reagent added was increased. Using another shift reagent,  $\text{Pr}(\text{FOD})_3\text{-d}_{27}$ , or changing the solvent ( $\text{CDCl}_3$ ) did not improve the result.

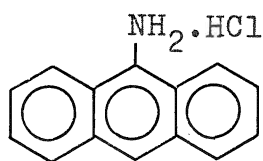
It was interesting to reexamine Schiedt's experiment under <sup>the</sup> same conditions (4 hours reflux), and also for longer time





Assuming that (93) was in fact the involved intermediate, it seemed most likely that the hydroxyl-group occupied position 10, as this is the most reactive position in the system. However, attempts were made to specify the position of -OH group. In order to distinguish between position 10 and others, (94) was treated with hydrogen peroxide in basic medium. According to Hassall and Morgan's procedure<sup>82</sup>, an oxidation to anthraquinone would confirm compound (94) as 10-hydroxy-9-N-formylaminoanthracene. However, the reaction of (94) with this reagent was comparatively slow; chromatography of the crude product (Benzene/Florisil) gave pure anthraquinone in 37.4% yield, with recovery of 24% of unchanged starting material.

To determine whether (93) was involved as an intermediate in the formation of (94), it was decided to examine the reaction of (93) with formamide. However, a commercial sample of 9-aminoanthracene-hydrochloride (95) required for preparation of (93) was found to be impossible as a source of pure 9-aminoanthracene (or its hydrochloride salt, 95), and the reaction could not therefore be examined.



(95)

The commercial sample when treated with 2N NaOH was found to contain, at least, four major components (t.l.c., benzene-silica gel). The commercial sample was separately extracted with hot benzene and the extract was chromatographed (Florisil/Benzene) to give pure 9,10-dichloroanthracene (10.5%) (m.p. 210-210.5°, Lit.<sup>78</sup> 210°); the mass spectrum showed molecular ion at  $m/e$  246 with reasonable isotopic abundance corresponding to two chlorine atoms cluster. The source of this compound in the commercial material is not clear.

The effect of formic acid in accelerating the reductive displacement of the N-formylamino-group at least for compounds derived from some of the chloroanthraquinones has been referred to above (for example, 85 and 87 under this treatment gave 86 and 88 respectively). It was considered only of marginal interest to examine the behaviour of Schiedt's compound (82) on treatment with formic acid and formamide in view of the lower reactivity of anthraquinones lacking a 1-chloro-substituent in the overall reaction. In fact, Schiedt's compound was mainly unchanged when treated with formic acid in formamide, possibly because it is insoluble in the hot mixture and precipitated from hot formamide when formic acid was added. One curious feature, not yet explained,

is the conversion of (82) to (94) by reaction with formamide and ammonium formate (p. 73).

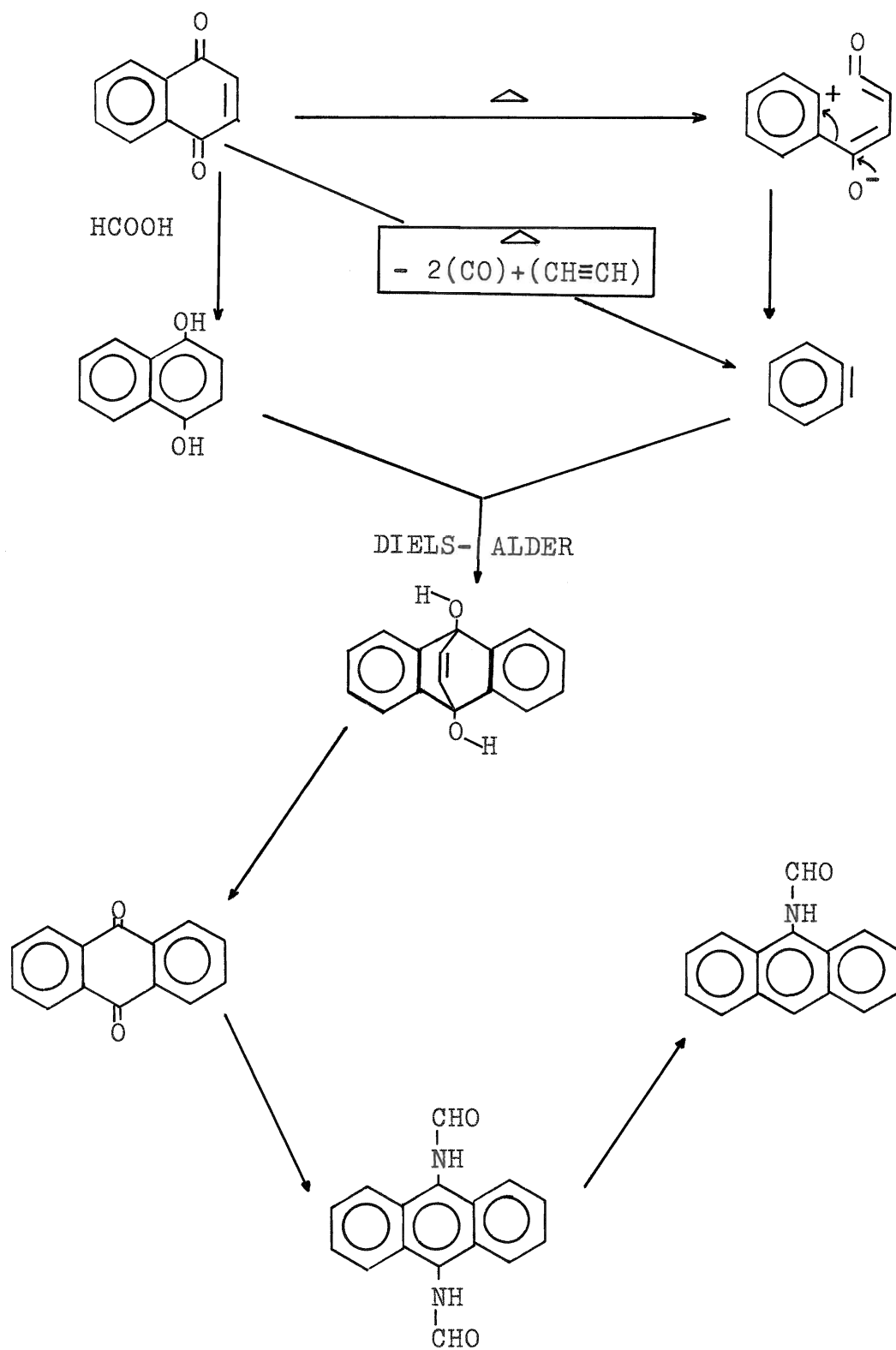
To conclude this phase of the work, experiments were carried out to study the behaviour of 1,4-naphthoquinone and 1,4-benzoquinone on similar treatment with formamide. When 1,4-naphthoquinone was treated with formamide, a fast reaction<sup>occurred</sup> even at room temperature. Two hours at reflux gave a black mixture which was extracted with ethanol and the soluble material was chromatographed to give the unexpected products (82) in 28.4% and (93) in 2%. The mass spectrum of the black residue remaining from the ethanol extraction showed a spectrum identical with that of an authentic sample of anthraquinone. However, this residue looked like charcoal and benzene extraction failed to isolate the anthraquinone. The sample of 1,4-naphthoquinone used in this experiment was purified (m.p. 128°) and had a reasonable mass spectrum.

Although it is of interest to know how this reaction proceeds, it is not a useful reaction for making these isolated compounds. Attempts were not made to study the mechanism of the reaction, though a suggestion is offered in scheme (19).

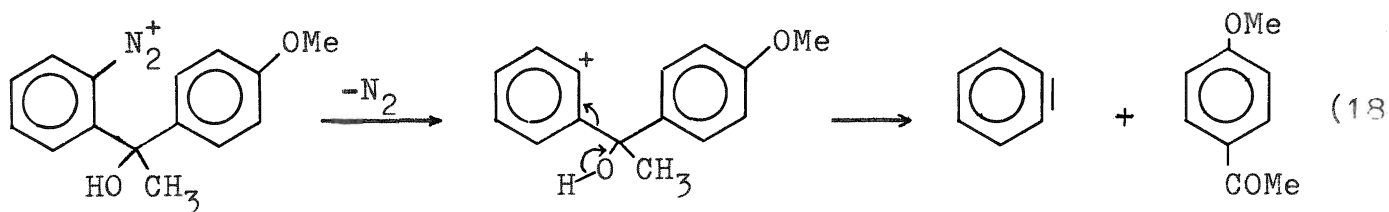
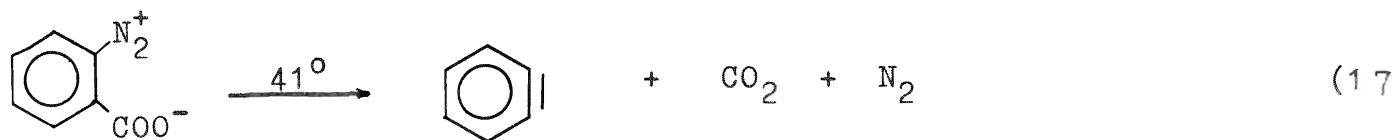
Four facts which might support this suggestion (scheme 19) are :

1. Generation of benzyne, under quite mild conditions in some cases (equation 17) is well established. For a review, see Hoffmann<sup>2</sup>. The following examples are illustrative :-

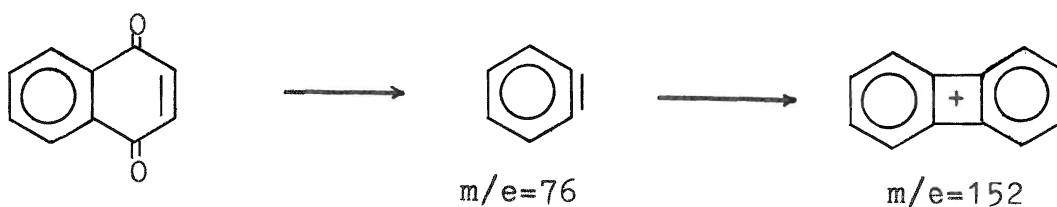
Scheme (19)







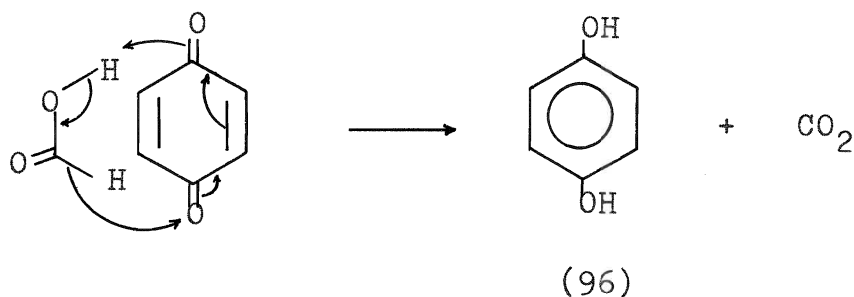
2. Examination of the mass spectrum of 1,4-naphthoquinone<sup>69</sup> suggests the presence of benzyne and biphenylene species.



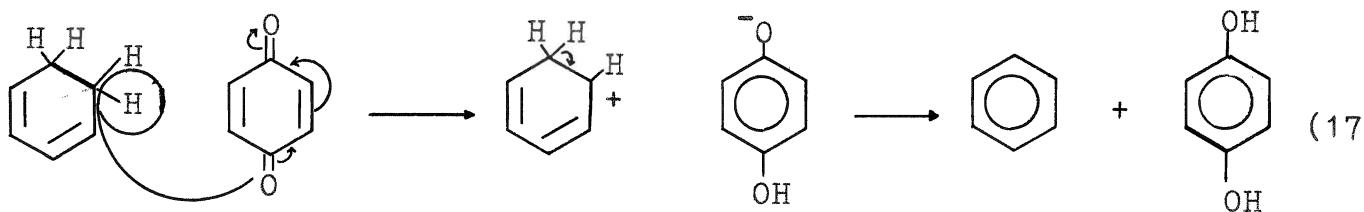
3. As was mentioned earlier, anthraquinone gave the same product (82) under this treatment.

4. The reaction of 1,4-benzoquinone with formamide was

examined by this writer, and shown to give hydroquinone (96) (see below). This supports the possible formation, by analogy, of 1,4-dihydroxynaphthalene from 1,4-naphthoquinone under these conditions.



Treatment of 1,4-benzoquinone with formamide resulted in a vigorous reaction and a large quantity of tar. Ethanol extraction of the tarry product gave an oily black material which afforded a black solid on dilution with a small quantity of acetone. Sublimation of this black solid gave 1,4-hydroquinone(13.7%), m.p.  $169^{\circ}$ . The mass spectrum of hydroquinone is fortunately very characteristic<sup>69</sup> and different enough from that of the starting material to prevent any confusion. This result in itself is not surprising, since 1,4-benzoquinone is often used as dehydrogenating agent. For a review see Jackman<sup>75</sup>. An example is shown in equation (17).



These reactions of 1,4-naphthoquinone and 1,4-benzoquinone,

although not synthetically useful, show that not every p-quinone behaves under this treatment as anthraquinones do.

#### CONCLUSIONS.

N-Methylacridone-1-carboxylic acid and related compounds can thus in principle be prepared from a variety of 5-chloro-1-N-methylaminoanthraquinones. This convenient two-stage synthesis would seem to be a useful new approach to various acridone derivatives since the procedure involves basic conditions and low temperatures.

Although further work is necessary, the route looks very promising for analogous syntheses of xanthenes and thioxanthenes.

The synthesis of various anthracenes (Such as 1,5-dichloro-, 1,8-dichloro- and 1-chloroanthracenes) that has been developed from corresponding anthraquinones looks promising for large scale use. The method is a very convenient one-stage synthesis and may well be one of the best available methods.

## EXPERIMENTAL

## INSTRUMENTATION AND TECHNIQUES

### 1. Melting Point.

These were measured on an "Electrothermal" m.p. apparatus. The values quoted are uncorrected.

### 2. Thin Layer Chromatography.

This was carried out using Silica Gel IB2-F sheets supplied by J.T.BAKER CHEMICAL CO. PHILLIPSBURG, N.J. 08865. The slides were examined under u.v. light and when necessary developed by exposure to iodine vapour.

### 3. Column Chromatography.

Unless otherwise stated all columns were packed with Florisil ( 60-100 mesh ).

### 4. Infra-red Spectra.

Compounds were mixed with potassium bromide and compressed into thin disks, from which spectra were obtained on a "Perkin Elmer (model 237B)" grating infra-red spectrophotometer.

### 5. Nuclear Magnetic Resonance Spectra.

The spectra were obtained on a "Varian A60" nuclear magnetic resonance spectrometer. Tetramethylsilane was used as internal reference. The solvents used are indicated in the text.

### 6. Mass Spectra.

The machine used to obtain these spectra was an A.E.I.-MS30, double beam, double focusing mass spectrometer. All the reported spectra were run at 70 e.v. unless otherwise indicated. The results are quoted as m/e values for the lowest isotopic species.

### 7. Yield.

Yields are based on material used for the reaction.

### 8. Microanalyses.

These were carried out by Dr. F. Pascher, Mikroanalytisches Laboratorium, Buschstr, 54, 5300 Bonn, Germany.

### 9. Solvents.

Tetrahydrofuran was dried over Aluminium Lithium Hydride and then distilled.

#### Preparation of Potassamide in liquid ammonia

#### Using liquid ammonia dried in situ (redistilled)

Commercial liquid ammonia was introduced into a 3-necked flask. Small chips of sodium were added, until the mixture attained a permanent blue colouration. A water bath was used to drive off the ammonia into a second 3-necked flask, fitted with a cold dry-ice condensor, a mechanical stirrer and a dropping funnel.

The ammonia was condensed with solid carbon dioxide in acetone. A small chip of potassium was added. This always turned the mixture deep blue. A small crystal of ferric nitrate was added followed by the requisite amount of potassium. The mixture was then stirred until the blue colour gave way to the grey of potassamide.

TREATMENT OF AROMATIC NITRO-COMPOUNDS WITH  
POTASSAMIDE IN LIQUID AMMONIA

4-NITROBENZOPHENONE.

4-Nitrobenzophenone (4.26 g., 0.0187 mole) dissolved in dry tetrahydrofuran (100 ml.) was added to a solution of potassamide prepared from potassium (3.9 g., 0.1 atom) and liquid ammonia (700 ml.) dried in situ. The mixture was stirred for 7 hours. Ammonium chloride (5 g.) and ether (100 ml.) were added. The ammonia was allowed to evaporate overnight. A brown solid remained.

The brown solid was treated with water (4 x 25 ml.) and filtered to give an aqueous solution (A) and a brown solid (B).

Solution (A) was acidified (4N HCl solution) and extracted with chloroform (4 x 50 ml.) to give an organic solution (C). This was evaporated to give a pale brown solid (3.2 g.) which was extracted with boiling water (30 ml.) to produce an aqueous solution (D) and a brown solid (E).

Solid (B) was extracted with chloroform (3 x 50 ml.) to give organic solution (F) and inorganic material.

Solution (F) was dried ( $\text{MgSO}_4$ ) and solvent was evaporated to give a crude product (2.9 g.) which was chromatographed (Florisil/Benzene) to give two fractions.

Fraction (I) was evaporated to give a yellow solid (1.9 g.), m.p. 129-132°; t.l.c. (Silica gel/Chloroform) showed the presence of unchanged starting material and a new material (G). The mass spectrum of (G), separated by t.l.c., showed molecular ion at

m/e 234. This was not identified and fraction (I) was not separated into its contents.

Fraction (II) was evaporated to give a yellow solid (0.8 g.) and was crystallized several times from aqueous ethanol to give pale yellow plates (0.3 g., 7%) of 3-amino-4-nitro-benzophenone, m.p. 200-201.5° (Lit.<sup>64</sup>, 199-200° and 200-201°); mass spectrum m/e 243(1)(M<sup>+</sup>), 242(8)(M<sup>+</sup>, C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>), 227(1)(M<sup>+</sup>-NH), 226(3)(M<sup>+</sup>-O<sup>+</sup>), 212(2)(M<sup>+</sup>-NO), 210(2), 196(0.3)(M<sup>+</sup>-NO<sub>2</sub>), 195(0.4), 181(1) M<sup>+</sup>-(NO<sub>2</sub>)-(NH), 167(1), 149(1)(O<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-CO<sup>+</sup>), 122(1)(O<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>), 105(100%)(C<sub>6</sub>H<sub>5</sub>-CO<sup>+</sup>), 77(56)(C<sub>6</sub>H<sub>5</sub><sup>+</sup>), .....etc.;  $\nu_{\max}$ . 3340(M), 1660(S), 1625(S), 1600(S), 1575(M), 1530-1480(S), 1405(S), 1345-1300(S), 1250(S), 1180(S), 1110(S), 1075(M), 865(M), 848(S), 750(S), 690(M), 720(S)<sub>A</sub><sup>cm<sup>-1</sup></sup>; a mixture m.p. with an authentic sample\* of 2-amino-4-nitrobenzophenone was 147-149°; t.l.c. (Silica gel/Chloroform) indicated that this reaction product was not 2-amino-4-nitrobenzophenone. The mass spectrum of the authentic sample of 2-amino-4-nitrobenzophenone showed m/e 243(11), 242(M<sup>+</sup>) (62), 241(73), 226(4), 225(6), 212(10), 211(24), 196(10), 195(26), 165(16), 105(100%), 77(61), .....etc.;  $\nu_{\max}$ . 3463(S), 3360(S), 3050(M), 1638(S), 1573(S), 1510(S), 1440(M), 1348(S), 1305-1320(M), 1250(S), 1185(W), 900(M), 823(M), 800(W), 760(M), 735(S), 715(S), 705(M), 660(M) cm<sup>-1</sup>.

On cooling, solution (D) deposited a white solid which was sublimed under reduced pressure to give colourless plates of pure benzoic acid (0.6 g., 31%), m.p. 122°, and mixture m.p. 121-122°; mass spectrum showed molecular ion at m/e 122;  $\nu_{\max}$ . 3040-2500(O-H str.), 1905, 1690(-C=O str.), 1605 and 1495 (C=C, Ar.), 1420, 1290, 935(-COOH) and 700 cm<sup>-1</sup>.



Solid (E) was washed with 2N NaOH solution (2X25 ml.), 2N HCl solution (3 X 25 ml.), extracted with hot chloroform (2 X 25 ml.) and the solvent was then evaporated (15 m.m.Hg) to give a product (0.135g., 3%) which was identified from the mass spectrum as 3-hydroxy-4-nitrobenzophenone (See discussion, p. 32). This was not purified.

\* Offered by Dr. K. Schofield, Dept. of Chemistry, University of Exeter, ENGLAND.

#### 4-NITRODIPHENYL SULFONE.

##### A. Preparation of 4-nitrodiphenyl sulfone.

##### (i) Preparation of 4-nitrodiphenyl sulfide.

(a) A solution of thiophenol (16.71 ml., 0.3 mole) in absolute ethanol (25 ml.) was added over 15 min. to a stirred solution of potassium ethoxide, prepared from potassium (11.7 g., 0.3 atom) and absolute ethanol (200 ml.). A solution of 4-fluoronitrobenzene (31.8 ml., 0.3 mole) in absolute ethanol (50 ml.) was added over 15 min. to the previously prepared thiophenoxide solution. The mixture was stirred under reflux for 10 hours and then cooled.

The cold reaction mixture was filtered to remove inorganic material and the solvent was evaporated under reduced pressure (15 m m.Hg) to give a crude product which was crystallised from ethanol (or ether or benzene) to give lemon yellow plates (97-99%) of 4-nitrodiphenyl sulfide, m.p. 54.5-55° (Lit.<sup>76</sup>, 55°); mass spectrum m/e 231(100%)(M<sup>+</sup>, C<sub>12</sub>H<sub>9</sub>SN<sub>2</sub>O), 215(4)(M<sup>+</sup>-O<sup>•</sup>), 201(14)(M<sup>+</sup>-NO), 185(76)(M<sup>+</sup>-NO<sub>2</sub>), 152(17), 141(7), 139(10), 114(14), 109(24), 77(25), 76(6), 65(27), 63(14), 58(3), 51(27), 45(17), 43(3), 39(11),....etc.

(b) The experiment was repeated with modifications. Thiophenol (5.57 ml., 0.1 mole) in absolute ethanol (25 ml.) was added over 15 min. to a stirred solution of potassium ethoxide, prepared from potassium (7.8 g., 0.2 atom) and absolute ethanol (200 ml.). A solution of 4-fluoronitrobenzene (10.6 ml., 0.1 mole) in absolute ethanol (25 ml.) was then added over 20 min. to the previously prepared thiophenoxide solution. The mixture was stirred under reflux for 15 hours.

The reaction mixture was allowed to stand at room temperature for 1 hour and then filtered to give a brown solid (A) and an ethanolic solution (B).

The crude solid (A)(3.75 g.) was crystallized from absolute ethanol to give bronze needles (3.2 g., 16%) of di(thio-phenoxy)azoxybenzene, m.p. 118-119° (Found: C, 69.33; H, 4.12; S, 15.57%.  $C_{24}H_{18}S_2N_2O$ . requires: C, 69.56; H, 4.34; S, 15.46%); mass spectrum m/e 417(6), 416(19), 415(37), 414( $M^+$ , 93%), 398(25), 374(6), 372(12), 370(6), 199(62), 198(56), 185(93), 184(100%,  $C_6H_5-S-C_6H_4^+$ ), 168(12), 152(19), 109(25), 105(90), 91(12), 90(87), 77(40), .....etc. ;  $\nu_{max}$ . 3025-3050(W)(broad), 1570-1585(S), 1530(W), 1475(S), 1450(S), 1438(M), 1385-1400(W), 1320(W), 1305(W), 1280(W), 1265(W), 1178(M), 1095(W), 1080(M), 1025(W), 1000-1010(W), 915(M), 830(S), 750(S), 705(M), 685(S), 660(M) $cm^{-1}$ , .....etc.

Ethanolic solution (B) was evaporated under reduced pressure (15 m.m.Hg) to give a brown solid (14.1 g.) which was crystallized from ethanol to give lemon yellow plates (10.5 g., 46%) of pure 4-nitrodiphenyl sulfide, m.p. 54.5-55° (mixture m.p. 54-55°); mass spectrum was identical with that of a sample from previous experiment.

(C) 4-Nitrodiphenyl sulfide (2.31 g., 0.01 mole) in absolute ethanol was added over 20 min. to a stirred solution of potassium ethoxide, prepared from potassium (0.39 g., 0.01 atom) and absolute ethanol (200 ml.). The mixture was stirred under reflux for 15 hours.

The reaction mixture was allowed to stand at room temperature for 1 hour and then filtered to give a brown solid (A) and an ethanolic solution (B).

The dry solid (A)(0.4 g.) was crystallized from absolute ethanol to give bronze needles (0.35 g., 17%) of di(thiophenoxy)-azoxybenzene, m.p. 118-119°; the  $R_f$  (chloroform), mass spectrum and i.r. spectrum were identical with those of the compound which was identified as di(thiophenoxy)azoxybenzene.

Solution (B) was evaporated under reduced pressure (15m.m. Hg) to give a brown solid was crystallized from ethanol to give lemon-yellow plates (1.8 g., 78%) of 4-nitrodiphenyl sulfide, m.p. 54-55°; the  $R_f$  (Chloroform) and mass spectrum were identical with these of the starting material.

(ii) Treatment of 4-nitrodiphenyl sulfide with hydrogen peroxide.

4-Nitrodiphenyl sulfide (11.55 g., 0.05 mole) was dissolved in glacial acetic acid (100 ml.) and a 30% solution of hydrogen peroxide (8.7 ml., 0.075 mole) was added. The mixture was digested on a steam bath for 5 hours and then poured into water (cooled and stirred). The precipitated sulfone (14.8 g.) was crystallized from absolute ethanol to give white plates (10.8 g., 82%) of pure 4-nitrodiphenyl sulfone, m.p. 142°(Lit.<sup>77</sup>, 78%; m.p. 142°); mass spectrum m/e 265(2), 264(5), 263( $M^+$ )(32), 247(0.5), 233(1), 217(1), 199(0.5), 186(0.5), 170(38), 152(9), 141(17), 138(0.5), 125(75), 122(0.5), 93(50), 77(100%),.....etc.

(B) Reaction of 4-nitrodiphenyl sulfone with potassamide in liquid ammonia.

(i) 4-Nitrodiphenyl sulfone (2.63 g., 0.01 mole) in dry ethanol (prepared by the standard method<sup>68</sup>) (75 ml.) was added over 20 min. to a solution of potassamide, prepared from potassium (7.8 g., 0.2 atom) and redistilled liquid ammonia (500 ml.). The mixture was stirred for 8 hours. Ammonium chloride (6 g.) and ether (100 ml.) were then added. The ammonia was allowed to evaporate overnight.

The reaction mixture was treated with water (3 x 25 ml.) and then filtered to give a solid (A) and an aqueous solution (B).

Solid (A) was extracted with ethanol (3 x 100 ml.) and filtered to give a dark brown solid (C) and an ethanolic solution (D).

Solid (C), m.p.  $\rangle 360^\circ$ , was found to contain only inorganic material.

Solution (D) was evaporated under reduced pressure (15 m. m.Hg) to give a pale yellow solid which was chromatographed on Florisil (benzene) to give two fractions.

Fraction (I) was evaporated to give a pale yellow solid (2.0 g.) which was crystallized from ethanol/benzene to give white plates (1.7 g., 65%) of 4-ethoxydiphenyl sulfone, m.p.  $114.5-115^\circ$  (Found: C, 63.99; H, 5.34%.  $C_{14}H_{14}SO_3$  requires: C, 64.11; H, 5.34%); mass spectrum m/e 264(5), 263(20), 262( $M^+$ ) (100%), 247(0.5), 234(4), 233(2), 198(0.5), 185(2), 170(3), 169(4), 157(4), 141(55), 137(5), 125(8), 126(35), 121(2), 110(30), 94(3), 93(3), 78(5), 77(8), 65(6), ....etc.;  $^1H$ -n.m.r.

spectrum ( $\text{CDCl}_3$ ): 8.0-6.8 $\delta$  (multiplet; 9H), 4.23, 4.13, 3.98 and 3.87  $\delta$  (quartet; 2H), 1.53, 1.42 and 1.28  $\delta$  (triplet; 3H).

Fraction (II) was evaporated. Crystallization from ethanol gave yellow prisms (0.49 g., 29%) of 4-ethoxynitrobenzene, m.p. 59-60 $^\circ$  (Lit.<sup>78</sup>, 60 $^\circ$ ); mass spectrum m/e 168(18), 167( $\text{M}^+$ )(100%), 151(5), 139(54), 123(5), 109(52), 93(8), 81(25), 65(44), ...etc.;  $^1\text{H}$ -n.m.r. ( $\text{CDCl}_3$ ): 8.2 and 8.07, 6.96 and 6.82  $\delta$  (two doublets; 4H), 4.29, 4.17, 4.05 and 3.94  $\delta$  (quartet; 2H), 1.54, 1.42 and 1.32  $\delta$  (triplet; 3H).

(ii) 4-Nitrodiphenyl sulfone (2.63 g., 0.01 mole) in dry tetrahydrofuran (50 ml.) was added over 15 min. to a solution of potassamide, prepared from potassium (3.9 g., 0.1 atom) and redistilled liquid ammonia (500 ml.). The mixture was stirred for 5 hours. Ammonium chloride (5 g.) and ether (100 ml.) were then added. The ammonia was allowed to evaporate overnight.

The reaction mixture was treated with water (4 x 50 ml.) and then filtered to give a brown solid (A) and an aqueous solution (B).

Solid (A) was dissolved in benzene and chromatographed (Florisil/Benzene) to give two fractions.

Fraction (I) was evaporated. Crystallization from ethanol-benzene (3:1) gave white needles (256 mg., 11%) of 4-aminodiphenyl sulfone, m.p. 176 $^\circ$  (Lit.<sup>76</sup>, 176 $^\circ$ ); mass spectrum m/e 235(9), 234(15), 233( $\text{M}^+$ )(96), 206(2), 169(16), 156(18), 152(3), 141(16), 140(43), 125(11), 108(98), 93(27), 92(61), 78(100%), 77(79), ...etc.

Fraction (II) was evaporated to give a pale brown solid

(97 mg.) which melted at  $145^{\circ}$  and thought to be 4-nitroaniline (Lit.<sup>78</sup>, m.p.  $147.8^{\circ}$  cor.); mass spectrum m/e 138 ( $M^{+}$ ); t.l.c. (Chloroform)(Same  $R_f$  as that of a sample of a commercial 4-nitroaniline). This could not<sup>be</sup> obtained in pure condition.

The aqueous solution (B) was acidified ( 2N HCl ) and then extracted with ether. The etherial solution was dried ( $MgSO_4$ ) and evaporated (15 m.m.Hg.) to give yellow solid (267 mg.). Thin layer chromatography of this solid showed the presence of 4-aminodiphenyl sulfone and 4-nitroaniline together with a quantity of tar. These were not purified.

#### 4-NITRODIPHENYL SULFIDE.

4-Nitrodiphenyl sulfide (5.8 g., 0.025 mole) in dry tetrahydrofuran (75 ml.) was added to a solution of potassamide, prepared from potassium (3.9 g., 0.1 atom) and liquid ammonia (500 ml.) dried in situ.

The mixture was stirred for 4 hours. Ammonium chloride (5 g.) and ether (100 ml.) were added. The ammonia was allowed to evaporate overnight. A brown solid remained.

The brown solid was extracted with hot ethanol (5 x 50 ml.) to give an ethanolic solution (A) and brown solid (B).

Thin layer chromatography (Benzene/Silica gel) of ethanolic solution (A) showed the presence of five components. Ethanol was evaporated to give a crude product (3.62 g.) which was extracted with warm benzene (5 x 25 ml.). The benzene extract was chromatographed (Florisil/benzene) to give three fractions.

Fraction (I) was evaporated. Crystallization from ethanol gave yellow needles (1.5 g., 36%) of 4-ethoxy-2-hydroxynitrobenzene, m.p.  $107^{\circ}$  (Found: C,       ; H,       %.  $C_8H_9NO_4$ . requires: C, 52.46; H, 4.92%); mass spectrum m/e 184 (2), 183( $M^+$ )(20), 182(100%), 168(1), 167(5), 166(6), 155(4), 154(30), 152(6), 138(11), 136(6), 124(93), 108(66), 96(59),...etc.;  $^1H$ -n.m.r. ( $CDCl_3$ ): 8.14 and 7.96  $\delta$  (doublet; 1H), 6.38-6.0  $\delta$  (multiplet; 3H), 4.21, 4.1, 3.97 and 3.87  $\delta$  (quartet; 2H), 1.53, 1.42 and 1.3  $\delta$  (triplet; 3H).

Fraction (II) was evaporated. Crystallization from ethanol gave yellow prisms (334 mg., 8%) of 4-ethoxynitrobenzene, m.p.  $59-60^{\circ}$  (Lit.<sup>78</sup>,  $60^{\circ}$ ); the mass spectrum was identical with that of a sample which was identified in<sup>a</sup> previous experiment as 4-ethoxynitrobenzene.

Fraction (III) was obtained as an oily red material (1.4 g.). This was found to be a mixture of two unidentified components.

### NITROBENZENE.

Nitrobenzene (6.15 g., 0.05 mole) in dry tetrahydrofuran (100 ml.) was added dropwise to a solution of potassamide, prepared from potassium (3.9 g., 0.1 atom) and liquid ammonia (500 ml.) dried in situ.

The mixture was stirred for 4 hours. Ammonium chloride (5 g.) and ether (100 ml.) were added. The ammonia was allowed to evaporate overnight.

The reaction mixture was extracted with hot ethanol (3 x 50 ml.) to give an ethanolic solution (A) and solid (B).



Thin layer chromatography (Silica gel/benzene) of the extract (A) showed the presence of 6 components. Evaporation of the solvent gave a crude product (5.9 g.) which showed in mass spectrometry molecular ions at  $m/e$  198, 170, 152 and 139 a.m.u. with reasonable fragmentation peaks corresponding to X-ethoxybiphenyl, X-phenylphenol, biphenylene and X-nitrophenol in ratio 7:1.5:1.7:1 respectively. The benzene extract of the crude product was chromatographed (Florisil/benzene) to give two fractions.

Fraction (I) was obtained as <sup>an</sup> orange solid which was crystallized from ethanol to give orange needles (3 g., 35%) of (probably) 2-phenylphenol, m.p.  $57^{\circ}$  (Lit.<sup>78</sup>,  $57^{\circ}$ ) (Found: C, ; H, %).  $C_{12}H_{10}O$ . requires: C, 84.71; H, 5.88 %); mass spectrum  $m/e$  170( $M^+$ )(3), 169(5), 152(3), 141(6), 91(36), 77 (100%), ...etc. ;  $^1H$ -n.m.r. ( $CDCl_3$ ): 8.04-7.7  $\delta$  (multiplet, 4H), 7.63-7.26  $\delta$  (multiplet, 6H).

Fraction (II) was obtained as a mixture of two unidentified materials which are thought to be 2-ethoxybiphenyl and possibly biphenylene ( $m/e$ , 198 and 152 respectively). This mixture (2.1 g.) was not separated into its constituents.

4-NITROTOLUENE.

4-Nitrotoluene (2.75 g., 0.02 mole) in dry tetrahydrofuran (50 ml.) was added over 20 min. to a solution of potassium amide, prepared from potassium (2.34 g., 0.06 atom) and redistilled liquid ammonia (400 ml.). The purple mixture was stirred for 4 hours. Ammonium chloride (6 g.) and ether (100 ml.) were then added. The ammonia was allowed to evaporate overnight.

The brown mixture was treated with water (2 x 50 ml.) and then filtered to give a solid (A) and an aqueous solution (B).

Solution (B) was extracted with ether (100 ml.) to give ethereal solution (C) and aqueous solution (D).

Solution (D) was evaporated under reduced pressure to give inorganic material (6 g.) which did not melt below 360°.

Solution (C) was dried (MgSO<sub>4</sub>) and evaporated to give an oily material (0.2 g.) which contained 5 components (t.l.c., chloroform/silica gel) including starting material.

Solid (A) was extracted with hot glacial acetic acid (150 ml.) and filtered to give a clear acidic solution (E) and a yellow residue (F)(0.4 g., 15%).

Solution (E) was diluted with water to produce a pale yellow amorphous powder (2.2 g., 80%) which was dried and crystallized from benzene to give yellow needles (2.1 g., 77%) of 4,4'-dinitrobibenzyl, m.p. 178.5-180° (Lit.<sup>78</sup>, 176-178°; needles or slender prisms, m.p.<sup>23</sup> 179.5-180.5°); mass spectrum m/e 272 (M<sup>+</sup>)(50), 256(7), 242(1), 226(15), 178(16), 165(11), 152(9), 136(100%) (O<sub>2</sub>N.C<sub>6</sub>H<sub>4</sub>.CH<sub>2</sub>), 120(17), 106(67), 90(58), 78(83), 77(17), 76(20), ...etc. ;  $\nu_{\text{max}}$ . 2920(C-H str.), 1610 and 1590(C=C str., Ar.), 1500 and 1335(N-O str.), 1106, 850(C-N str.), 782, 750

and  $695\text{ cm}^{-1}$ .

Residue (F) was crystallized from ethanol and identified as 4,4'-dinitrostilbene, m.p.  $292-293^{\circ}$  (Lit.<sup>81</sup>,  $294-295^{\circ}$ ); mass spectrum  $m/e$  270( $M^{+}$ )(32), 254(5), 240(31), 224(4), 210(100%) ( $M^{+}-2NO$ ), 194(19), 178(20), 165(31), 152(13), 136(14), 120(5), 106(46), 91(13), 90(12), 89(11), 78(11), 77(13), 76(14), 65(13), 63(12), 51(12), 44(20), 39(11), 28(54), 18(91).

#### 4,4'-DINITROBIBENZYL.

4,4'-Dinitrobibenzyl (2.2 g., 0.0081 mole) in dry tetrahydrofuran (50 ml.) was added over 15 min. to a stirred solution of potassamide, prepared from potassium (5.5 g., 0.1410 atom) and redistilled liquid ammonia (700 ml.). The mixture was stirred for 4 hours. Ammonium chloride (5 g.) and ether (100 ml.) were then added. The ammonia was allowed to evaporate overnight.

The reaction mixture was treated with water (2 x 50 ml.) and then filtered to give a solid (A) and an aqueous solution (B). Solid (A) was extracted with hot glacial acetic acid to give a yellow residue (C) and a clear acidic solution (D). Solid (C) was crystallized from ethanol to give 4,4'-dinitrostilbene (1.6 g., 73%), m.p.  $292-293^{\circ}$  (Found: C, 61.93; H, 3.64; N, 10.20%.  $C_{14}H_{10}N_2O_4$  requires: C, 62.22; H, 3.70; N, 10.37%); mixture m.p. with 4,4'-dinitrostilbene produced as by-product in the reaction of 4-nitrotoluene with potassamide showed no depression and the  $R_f$  values and mass spectra of the samples were identical.

Solution (D) was diluted with water and then filtered to produce a yellow solid (0.6 g., 27.3%); t.l.c.(chloroform) showed that this consisted mainly of 4,4'-dinitrostilbene and some unchanged starting material. This mixture was not separated into its constituents.

## 2-NITROTOLUENE.

2-Nitrotoluene (2.75 g., 0.02 mole) in dry tetrahydrofuran (50 ml.) was added over 15 min. to a solution of potassium amide, prepared from potassium (2.1 g., 0.0538 atom) and redistilled liquid ammonia (400 ml.). The reaction mixture was stirred for 4 hours. Ammonium chloride (5 g.) and ether (100 ml.) were then added. The ammonia was allowed to evaporate overnight.

The reaction mixture was treated with water (2 x 50 ml.) and then filtered to give a solid (A) and an aqueous solution (B). Solid (A) was extracted with hot glacial acetic acid; water was added to produce a brown-yellow solid which was filtered off and dried (1.6 g., m.p. 105-110°). Crystallization from chloroform produced yellow prisms (1.3 g., 48%) of 2,2'-dinitro-bibenzyl, m.p. 119-120° (Lit. , 123°, 122-123°, 122°, 120-121°) (Found: C, 61.76; H, 4.79%.  $C_{14}H_{12}N_2O_4$  requires: C, 61.76; H, 4.78%); mass spectrum  $m/e$  272( $M^+$ )(1), 255(7), 256(2), 242(3), 238(7), 237(8), 221(4), 220(5), 208(9), 206(7), 193(6), 178(17), 165(16), 152(17), 136(100%)( $O_2N.C_6H_4.CH_2$ ), 120(66), 106(37), ...etc.;  $\nu_{max}$ . 2920(C-H str.), 1610(C=C str., Ar.), 1503 and 1345(N-O str.), 860(C-N str.), 782, 748 and 695  $cm^{-1}$ .

The experiment was repeated. 2-Nitrotoluene (2.75 g., 0.02 mole) in dry tetrahydrofuran (50 ml.) was added over 15 min. to a solution of potassamide, prepared from potassium (11.7 g., 0.3 atom) and redistilled liquid ammonia (650 ml.). The reaction mixture was stirred for 12 hours. Ammonium chloride (10 g.) and ether (100 ml.) were then added. The ammonia was allowed to evaporate overnight.

The reaction mixture was treated with water (2 x 50 ml.) and then filtered to give a solid (A) and an aqueous solution (B).

Solid (A) was extracted with hot glacial acetic acid and filtered to give a solid (C) and an acidic solution (D).

Solid (C) was crystallized from chloroform to give yellow prisms (0.6 g., 22%) of 2,2'-dinitrobibenzyl, m.p. 118-119.5°; the mass spectrum showed fragmentation peaks with ratios similar to those described earlier for 2,2'-dinitrobibenzyl.

Solution (D) was diluted with water, allowed to stand for one hour and then filtered to give a yellow precipitate (1.6 g., 59%) of 2,2'-dinitrobibenzyl, m.p. 119-120°; t.l.c. (chloroform), mass spectrum and i.r. spectrum confirmed identity as 2,2'-dinitrobibenzyl.

#### 2-NITRO-1,3,5-TRIMETHYLBENZENE.

2-Nitro-1,3,5-trimethylbenzene (3.3 g., 0.02 mole) dissolved in dry tetrahydrofuran (50 ml.) was added to a solution of potassamide, prepared from potassium (7.8 g., 0.2 atom) and liquid ammonia (500 ml.) dried in situ.

The mixture was stirred for 6 hours. Ammonium chloride

(5 g.) and ether (50 ml.) were added. The ammonia was allowed to evaporate overnight.

The reaction mixture was treated with water (4 x 25 ml.) and filtered to give an aqueous solution (A) and a solid (B).

Solid (B) was extracted with hot glacial acetic acid (200 ml.) and filtered to give an acidic solution (C) and solid (D).

Solution (C) was poured into water (500 ml.) and then filtered to give a yellow solid (0.96 g., 30%), m.p. 159-160°; t.l.c. (chloroform) showed two spots and the mass spectrum showed a material (E) of molecular weight 238 a.m.u. together with unchanged starting material. Material (E) ( $C_{18}H_{22}$ ) was found in the commercial 2-nitro-1,3,5-trimethylbenzene (t.l.c./chloroform, and mass spectrum). Compound (E) is probably 2,2',4,4',6,6'-hexamethylbiphenyl. This mixture was not separated into its constituents.

Solid (D) was boiled with water for 2 hours, then washed with ethanol (4 x 100 ml.) and dried to give a brown material (1.95 g., 59%), m.p.  $> 300^\circ$ , which was identified as X,X'-dinitro-3,3',5,5'-tetramethylstilbene (Found: C, 66.55; H, 5.41; N, 9.09%.  $C_{18}H_{18}N_2O_4$  requires: C, 66.26; H, 5.52; N, 8.59%); mass spectrum m/e 326( $M^+$ ) (5), 168(100%), 150(18), 149(7), 138(28), 128(10), 125(5), 119(18), 118(20), 100(90), 93(21), ...etc.;  $\nu_{max}$ . 2825-2935(S), 1600(W, broad), 1450(S), 1375(S), 1300(W), 960(W), 720(M), ...etc.

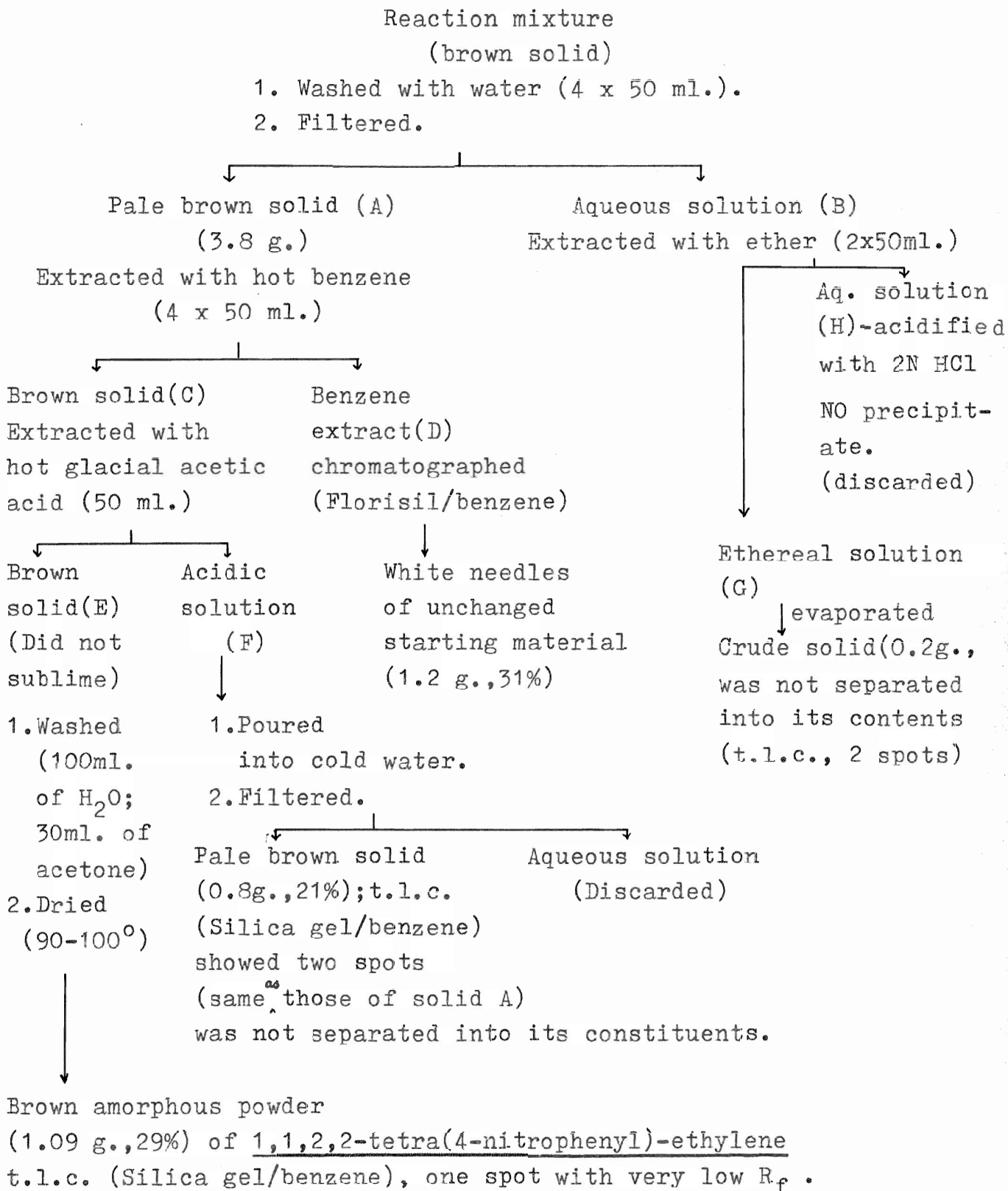
4,4'-DINITRODIPHENYLMETHANE.

A commercial sample of 4,4'-dinitrodiphenylmethane was successfully crystallized from benzene to remove a material showing molecular ion of 272 a.m.u. (thought to be 4,4'-dinitro-bibenzyl; same  $R_f$ ).

4,4'-Dinitrodiphenylmethane (3.87 g., 0.015 mole) in dry tetrahydrofuran (125 ml.) was added over 20 min. to a solution of potassamide, prepared from potassium (3.9 g., 0.1 atom) and liquid ammonia (600 ml.) dried in situ.

The mixture was stirred for 4 hours. Ammonium chloride (5 g.) and ether (100 ml.) were added. The ammonia was allowed to evaporate overnight. A brown solid remained.

The brown solid was worked-up as shown in diagram (II) to give a brown amorphous powder (1.09 g.) which was identified as 1,1,2,2-tetra(4-nitrophenyl)-ethylene, m.p.  $> 300^\circ$ ; mass spectrum  $m/e$  512( $M^+$ );  $\nu_{\max}$ . 3000-3500(W, broad), 2900(W), 2500-2750(W, broad), 1620-1675(S), 1585(M), 1515(M), 1400-1435(M), 1340(S), 1270(W), 1110(W), 1005(W), 850(W), 830(M), 745(W), 700(M)  $\text{cm}^{-1}$ .

Diagram II :



TREATMENT OF 1,5-DICHLOROANTHRAQUINONE WITH N-METHYLFORMAMIDE(i) PREPARATION OF 1,5-bis-(N-METHYLAMINO)-ANTHRAQUINONE.

1,5-Dichloroanthraquinone (3.4 g., 0.0123 mole) and N-methylformamide (30 ml.) were refluxed for 24 hours.

The reaction mixture was allowed to stand at room temperature for three hours and then filtered to give solid (A) and solution (B).

Solid (A)(2.3 g.) was crystallized from acetone to give dark red prisms with golden luster (2.1 g., 64%) of 1,5-bis(N-methylamino)anthraquinone, m.p. 218-220° (Lit.<sup>32</sup>, 218-220°); mass spectrum m/e 267(28), 266(M<sup>+</sup>)(100%), 249(55), 237(10), 236(11), 234(20), 221(7), 220(12), 209(6), 193(4), 180(6), 165(10), 153(8), 134(12), 77(5), ...etc.

Solution (B) was poured into water, and the precipitated solid (0.925 g.) was chromatographed (Florisil/benzene-ligroin, 1:1) to give dark red prisms with golden luster (0.8 g., 25%) of pure 1,5-bis(N-methylamino)anthraquinone, m.p. 218-220°; mixture m.p. 218°; R<sub>f</sub> (benzene) and mass spectrum were identical with those of the above sample of 1,5-bis(N-methylamino)anthraquinone.

(ii) PREPARATION OF 5-CHLORO-1-N-METHYLAMINOANTHRAQUINONE.

1,5-Dichloroanthraquinone (3.4 g., 0.0123 mole) and N-methylformamide (20 ml.) were refluxed for three hours.

The reaction mixture was allowed to stand at room temperature for about 12 hours and then filtered to give a

cherry red solid (3.2-3.3 g.) which was chromatographed on a long column of Florisil (benzene/ligroin) to give two fractions.

Fraction (I) gave, on evaporation, yellow needles (1.7-2.0 g.) of 1,5-dichloroanthraquinone, m.p.  $251^{\circ}$ ;  $R_f$  and mass spectrum were identical with these of the starting material.

Fraction (II) gave, on evaporation, long dark red needles (1.2-1.5 g., 35-43%) of 5-chloro-1-N-methylamino-anthraquinone, m.p.  $205.5-206.5^{\circ}$  (Lit.<sup>31</sup>,  $194-196^{\circ}$ ; Lit.<sup>32</sup>,  $196-197^{\circ}$ ); further crystallization from chloroform did not change the m.p. ( $205.5-206.5^{\circ}$ ); mass spectrum m/e 273(34), 271 ( $M^+$ )(100%), 256(17), 254(48), 245(4), 243(10), 236(14), 217(4), 216(6), 215(10), 214(17), 201(24), 199(71), 188(7), 186(20), 151(27), ...etc.;  $\nu_{\max}$ . 2800-2950(W, broad), 1730(M), 1668(S), 1625(S), 1590(S), 1570(S), 1510(S), 1450(W), 1425(W), 1400(W), 1365(W), 1320(S), 1260(S), 1205(M), 1175(M), 1135(W), 1085(W), 1070(W), 1010(W), 815(S), 765(S), 735(M),  $710(S)_{\lambda}^{cm^{-1}}$ ;  $^1H$ -n.m.r. ( $CDCl_3$ ): 8.3-6.8 $\delta$ (multiplet; 6H), 3.0  $\delta$  (doublet; 3H), 1.3  $\delta$  (singlet; 1H);  $^1H$ -n.m.r. ( $CDCl_3+D_2O$ ): 8.3-6.8  $\delta$  (multiplet; 6H), 3.0  $\delta$  (singlet; 3H).

#### REACTION OF 5-CHLORO-1-N-METHYLAMINOANTHRAQUINONE WITH POTASSAMIDE IN LIQUID AMMONIA.

5-Chloro-1-N-methylaminoanthraquinone (1.35 g., 0.005 mole) in dry tetrahydrofuran (100 ml.) was added over 20 min. to a solution of potassamide, prepared from potassium (3.9 g., 0.1 atom) and redistilled liquid ammonia (500 ml.). The red mixture was stirred for 4 hours. Ammonium chloride (5 g.) and

ether (75 ml.) were then added. The ammonia was allowed to evaporate overnight.

The residue was treated with 2N hydrochloric acid (4 x 50 ml.) and extracted with ether (3 x 100 ml.) to give an ethereal solution (A) and an acidic solution (B).

Solution (A) was extracted with 40% w/v sodium hydroxide solution (3 x 50 ml.) to give basic solution (C) and an ethereal solution (D).

Solution (B) was made alkaline by adding 40% w/v sodium hydroxide solution when a dark red solid (1.5 g.) separated; this was collected and extracted with chloroform (4 x 50 ml.) to give an inorganic material (1.3 g.) and a chloroform solution which was washed with water (3 x 25 ml.), dried ( $\text{MgSO}_4$ ), and evaporated under reduced pressure (15 m.m.) to give a crude red solid (0.18 g.). This was crystallized from ethanol (95%) to give red needles (0.15 g., 11%) of impure starting material, m.p. 141-158°; chromatography (Florisil/benzene) separated an unidentified yellow material (0.03 g.) from unchanged starting material which was found to be contaminated with a material showing m/e 253( $\text{M}^+$ ).

Solution (C) was acidified with 2N hydrochloric acid. No solid was produced. The solution was discarded.

Solution (D) was washed with water (2 x 50 ml.), dried ( $\text{MgSO}_4$ ), and evaporated to give a dark red solid (0.88 g., 65%) which was chromatographed (Florisil/benzene) to give red needles (0.63 g., 47%) of N-methylacridone-1-carboxylic acid

(crystallized from benzene as a solvate), m.p. 141-143°  
 (Found: C, 74.85; H, 5.23; N, 4.55%.  $C_{15}H_{11}NO_3 + C_4H_4$  requires:  
 C, 74.75; H, 4.92; N, 4.59%); mass spectrum  $m/e$  253( $M^+$ )(4), 252(7),  
 237(100%)( $M^+ - H^+ - Me^+$ ), 220(61), 209(19), 208(38), 180(74), 165  
 (19), 152(77), 151(64), ...etc. (see the Discussion, p. 58);  $\nu_{max}$ .  
 3280(W, broad), 2800-2960(M, broad), 1670(S), 1625(S), 1590(S),  
 1565(S), 1505(S), 1460(W), 1445(W), 1425(W), 1390(W), 1360(M),  
 1315(S), 1265(S), 1230(M), 1180(M), 1150(W), 1070(M), 985(M),  
 860(M), 825(S), 805(S), 775(W), 760(W), 735(S), 700(S), 660  
 (W)  $cm^{-1}$ ;  $^1H$ -n.m.r. ( $CDCl_3$ ): 10.0  $\delta$  (broad absorption; 1H) (exch-  
 angable with  $D_2O$ ), 8.3-6.8  $\delta$  (multiplet; 7H), 3.05  $\delta$  (singlet; 3H).

REACTION OF 5-CHLORO-1-N-METHYLAMINOANTHRAQUINONE WITH  
 POTASSIUM t-BUTOXIDE IN t-BUTYLBENZENE.

(A) Preparation of potassium t-butoxide.

Anhydrous t-butanol was prepared by refluxing the commercial product with sodium until about two-thirds of the metal had dissolved (~4 hours) and then distilled.

Dry nitrogen was prepared by passing through a train consisting of (a) a trap, (b) a wash bottle containing conc.  $H_2SO_4$ , and (c) a drying tube containing fresh soda lime.

Potassium (1.3 g., 0.033 atom) was slowly added to a 100 ml. three-necked-flask, equipped with condensor and drying tube, and inlet for nitrogen gas, containing t-butanol (24 g., 0.33 mole). The mixture was stirred for 8 hours; the hydrogen evolved escaped through the mercury trap.

The reaction mixture was washed with anhydrous ether (10 x 25 ml.) to remove the excess of t-butanol; the crude product (3.7 g., quantitative yield) was kept dry for the next step.

(B) Treatment of 5-chloro-1-N-methylaminoanthraquinone with t-butoxide in t-butylbenzene.

A mixture of 5-chloro-1-N-methylaminoanthraquinone (0.813 g., 0.003 mole), potassium t-butoxide (1.68 g., 0.015 mole) and t-butylbenzene (40 ml.) were refluxed under nitrogen for 12 hours.

t-Butylbenzene was then evaporated under reduced pressure (15 m.m.); the crude product was extracted with chloroform (5 x 25 ml.) to give an organic solution (A) and a black residue which was found to contain only inorganic material.

Solution (A) was evaporated under reduced pressure (15 m.m.) to give a red solid (0.58 g., 77%) which was chromatographed on Florisil (benzene) to give two fractions.

Fraction (I) gave an unidentified yellow solid (0.017 g.).

Fraction (II) provided red needles (0.52 g., 69%) of N-methylacridone-1-carboxylic acid, m.p. 141-143<sup>o</sup>; mass spectrum, i.r. and n.m.r. spectra were identical with these of the previous sample of N-methylacridone-1-carboxylic acid.

THE TREATMENT OF 1,5-DICHLOROANTHRAQUINONE WITH SODIUM SULFHYDRATE.

1,5-Dichloroanthraquinone (8.28 g., 0.03 mole) and sodium sulfhydrate (1.68 g., 0.03 mole) in benzyl alcohol (100 ml.) were refluxed for 9 hours.

The reaction mixture was filtered to give a solution (A) and a solid (B).

Solution (A) was distilled to remove about 90% of the benzyl alcohol. Acetone (30 ml.) was added to the thick liquid which remained. A rust solid was precipitated. The precipitate was chromatographed (Silica gel/benzene) to give a small orange cubes (0.78 g., 10%) of di-(5-chloroanthraquinon-1-yl)-sulfide, m.p. 326-327° (Found: C, 65.34; H, 2.43; S, 6.25; Cl, 13.48 %.

$C_{28}H_{12}Cl_2SO_4$  requires: C, 65.37; H, 2.33; S, 6.23; Cl, 13.62%; mass spectrum m/e 518(3), 516(12), 514(17) ( $M^+$ ,  $^{32}S$ ), 275(33), 273(100%) ( $C_{14}H_6ClSO_2$ ) $^{+}$ , 240(14), 218(10), 206(12), 185(11), 173(13), 150(46), 105(38), 77(46), 75(48), ...etc.

Solid (B) (7 g.) was found to be unchanged starting material contaminated with an unidentified material which was found to be not di-(5-chloroanthraquinon-1-yl)-sulfide (t.l.c., silica gel/benzene). This mixture was not separated into its constituents.

THE TREATMENT OF CHLOROANTHRAQUINONES WITH  
FORMAMIDE.

1. 1,5-DICHLOROANTHRAQUINONE.

1,5-Dichloroanthraquinone (3.4 g., 0.0123 mole) and formamide (30 ml.) were stirred under reflux for 24 hours.

The reaction mixture was allowed to cool to room temperature and then filtered. The crude solid was extracted with chloroform. The chloroform extract was allowed to stand at room temperature for 24 hours and then filtered to give a yellow solid (A) and chloroform solution (B).

Crude solid (A) (0.26 g.) was crystallized from benzene to give yellow needles (0.2 g., 5.6%) of N-formyl-9-amino-1,5-dichloroanthracene, m.p. 273-4° (Found: C, 62.65; H, 3.20; N, 4.81%.  $C_{15}H_9Cl_2NO$ . requires: C, 62.28; H, 3.11; N, 4.84%); mass spectrum m/e 293(5), 291(21), 289(29) ( $M^+$ ,  $^{35}Cl$ ), 266(2), 265(5), 264(9), 263(23), 262(12), 261(32), 260(8), 256(14), 255(34), 254(35), 253(100%) ( $M^+ - HCl$ ,  $^{35}Cl$ ), 252(33), 238(1), 237(3), 236(2), 235(12), 234(3), 233(17), 229(4), 228(6), 227(12), 226(17), 225(5), 224(9), 220(20), 200(9), 198(26), 191(17), 190(42), .....etc.;  $\nu_{max}$ . 3220-3110(M), 2975-2850(W), 1645(S), 1515(M), 1495(M), 1440(S), 1380(M), 1340(M), 1215(W), 1195(M), 1040(W), 950(W), 885(M), 780(M), 740(W), 715(S), 690(M)  $cm^{-1}$ ).

Chloroform solution (B) was evaporated to give a crude product (1.8 g.) which was chromatographed on Florisil (benzene/ligroin) to give lemon yellow plates (0.9 g., 27%) of 1,5-dichloroanthracene, m.p. 186.5-187° (Lit.<sup>80</sup>, 187°) (Found: C, 67.97;

H, 3.32%.  $C_{14}H_8Cl_2$  requires: C, 68.29; H, 3.25%); mass spectrum  $m/e$  251(2), 250(14), 249(12), 248(71), 247(16) ( $MH^+$ ,  $^{35}Cl$ ), 246 (100%) ( $M^+$ ,  $^{35}Cl$ ), 215(1), 214(1), 213(4), 212(6), 211(6), 210 (8), 177(6), 176(31), 175(10), 174(10), 150(4), 124(10), 123(15), .....etc.;  $\nu_{max}$ . 1612(M), 1525(M), 1440(M), 1330(M), 1290(S), 1210(S), 1160(S), 960(S), 865(S), 775(S), 713(S)  $cm^{-1}$ .

2. The experiment was repeated with modifications. 1,5-Dichloroanthraquinone (3.4 g., 0.0123 mole) and formamide (30ml.) were stirred under reflux for 3 hours.

The reaction mixture was extracted with chloroform. The chloroform extract was evaporated and the residue chromatographed on Florisil (benzene/ligroin) to give three fractions.

Fraction (I) provided lemon-yellow plates (0.6 g., 20%), m.p.  $187^{\circ}$ ; mixture m.p.  $186.5-187^{\circ}$ , t.l.c. (Silica gel/chloroform), mass spectrum and i.r. spectrum indicated that this compound was 1,5-dichloroanthracene.

Fraction (II), obtained as yellow needles (1.02 g.), m.p.  $265-272^{\circ}$ , was crystallized from benzene to give pale yellow needles (0.95 g., 27%), m.p.  $273-274^{\circ}$ ; t.l.c. (Silica gel/benzene), mass spectrum and i.r. spectrum indicated that this compound was N-formyl-9-amino-1,5-dichloroanthracene.

Fraction (III) afforded unchanged 1,5-dichloroanthraquinone (1.35 g., 40%);  $R_f$ , mass spectrum and i.r. spectrum were identical with these of the starting material.



1-CHLOROANTHRAQUINONE.

1. 1-Chloroanthraquinone (9.0 g., 0.0372 mole) and formamide (100 ml.) were stirred under reflux for 8 hours.

The cold reaction mixture was filtered. The crude solid (10.1 g.) was crystallized from chloroform to give yellow needles of N-formyl-10-amino-1-chloroanthracene (9.5 g., 94%), m.p. 268.5-269° (Found: C, 68.74; H, 3.88; N, 5.36%.  $C_{15}H_{10}ClNO$  requires: C, 70.59; H, 3.92; N, 5.49 %); mass spectrum m/e 258(5), 257(24), 256(15) ( $M^+$ ), 255(72) ( $M^+$ ,  $^{35}Cl$ ), 230(8), 229(20), 228(26), 227(54), 226(23), 201(8), 199(26), 192(17), 190(20), 165(26), 58(51), 43(100%) (NHCO), 28(17) (CO), ...etc.;  $\nu_{max}$ . 3220-3130(M), 2880-2830(W), 1645(S), 1605(M), 1520(M), 1500(M), 1440(W), 1415(W), 1375(M), 1340(M), 1210(W), 1200(M), 1115(M), 950(S), 890(M), 885(M), 850(S), 790(S), 740(M), 720(M)  $cm^{-1}$ .

2. N-Formyl-10-amino-1-chloroanthracene (1.6 g., 0.0063 mole) and formamide (50 ml.) were refluxed for 16 hours.

The reaction mixture was poured into cold water. The precipitate was collected and extracted with hot ethanol to give ethanolic solution (A) and solid (B).

Solution (A) was evaporated and the solid which remained was extracted with benzene to give solution (C) and solid (D).

Solution (C) was chromatographed on Florisil (benzene) to give yellow plates of 1-chloroanthracene (0.12 g., 9%), m.p. 83-84° (Lit.<sup>78</sup>, 83.5°); mass spectrum m/e 214(11), 212(30) ( $M^+$ ), 177(5), 176(11), 151(6), 150(4), 126(2), 106(9), 88(14), 75(10),

58(60), 43(100%),...etc.

Solid (B) (1.2 g., 75%) was found to be unchanged starting material (t.l.c. and mass spectrum).

Thin layer chromatography (Silica gel/benzene) of solid (D) showed mainly unchanged starting material with a little 1-chloroanthracene. This mixture (0.1 g., 6%) was not separated into its constituents.

3. N-Formyl-10-amino-1-chloroanthracene (2.55 g., 0.01 mole), formic acid (20 ml.) and formamide (50 ml.) were refluxed for 9 hours.

The reaction mixture was filtered to give a crude solid (A) and a solution (B). Solid (A) was extracted with benzene (5 x 100 ml.) to give extract (C) and solid (D).

Benzene extract (C) was evaporated under reduced pressure and then chromatographed on alumina (benzene) to give yellow plates (0.41 g., 20%) of 1-chloroanthracene, m.p. 83-84°; mass spectrum was identical with that of the previous sample of 1-chloroanthracene.

Solid (D) (1.6 g., 65%) was found to be unchanged starting material contaminated with a little 1-chloroanthracene (t.l.c., mass spectrum). This was not purified.

Solution (B) was poured into cold water. The precipitate was collected (0.6 g., 7.9%) and found to be a mixture of unchanged starting material, 1-chloroanthracene and a little of unidentified material which is possibly N-formyl-9-amino-anthracene. This mixture was not separated into its constituents.

1,8-DICHLOROANTHRAQUINONE.

1. 1,8-Dichloroanthraquinone (8.3 g., 0.03 mole) and formamide (100 ml.) were refluxed for 3 hours.

The reaction mixture was poured into cold water. The precipitated solid was collected and washed with boiling water (3 x 100 ml.). The crude product was then crystallized from acetone to give yellow needles (8.3 g., 96%) of N-formyl-10-amino-1,8-dichloroanthracene, m.p. 307-10° (Found: C, ; H, ; N, %.  $C_{15}H_9Cl_2NO$ . requires: C, 62.28; H, 3.11; N, 4.84%); mass spectrum m/e 293(14), 291(55), 289( $M^+$ )(81), 261(100%), 233(63), 226(72), 199(90), 190(81), 163(90), ...etc.

2. The experiment was repeated with modifications. 1,8-Dichloroanthraquinone (13.85 g., 0.05 mole) and formamide (200 ml.) were refluxed for 6 hours.

The reaction mixture was worked-up as in experiment (1.) to give a yellow solid (10.6 g., 76%). Thin layer chromatography (Silica gel/benzene) showed two materials corresponding to N-formyl-10-amino-1,8-dichloroanthracene and 1,8-dichloroanthracene (A sample separated by t.l.c. showed molecular ion at m/e 212). This mixture was not separated into its constituents.

3. N-Formyl-10-amino-1,8-dichloroanthracene (1.5 g., 0.0052 mole) and formamide (50 ml.) were refluxed for 16 hours.

The reaction mixture was poured into water. The precipitate was collected, dried, and extracted with hot benzene

(4 x 100 ml.) to give extract (A) and solid (B).

Benzene extract (A) was evaporated under reduced pressure and then chromatographed on Florisil (benzene) to give yellow needles (0.174 g., 14%) of 1,8-dichloroanthracene, m.p.  $185^{\circ}$  (Lit.<sup>80</sup>,  $185^{\circ}$ ); mass spectrum m/e 246(100%)(M<sup>+</sup>), 211(7) (M<sup>+</sup>-<sup>35</sup>Cl), 210(9)(M<sup>+</sup>-HCl), 176(30)(M<sup>+</sup>-2Cl), 175(12)(M<sup>+</sup>-HCl<sub>2</sub>), 174(10)(M<sup>+</sup>-H<sub>2</sub>Cl<sub>2</sub>),...etc.;  $\nu_{\max}$ . 1615(S), 1525(M), 1435(M), 1335(M), 1295(S), 1208(M), 1165(S), 960(S), 860(S), 775(S), 715(S) cm<sup>-1</sup>.

Thin layer chromatography of the solid (B) (1.28 g., 85%) showed only unchanged starting material. The mass spectrum was identical with that of the previous sample. This was not purified.

4. N-Formyl-10-amino-1,8-dichloroanthracene (1.5 g., 0.0052 mole), formic acid (40 ml.) and formamide (50 ml.) were refluxed for 48 hours.

The experiment was worked-up as usual to give yellow needles (0.232 g., 18%) of 1,8-dichloroanthracene, m.p.  $185^{\circ}$ ;  $R_f$  and mass spectrum were identical with those of the previous sample. Unchanged starting material was recovered (1.2 g., 80%). This was found to be contaminated with a material showing molecular ion m/e 262 thought to be X-hydroxy-1,8-dichloro-anthracene. This was not isolated.

2-CHLOROANTHRAQUINONE.

1. 2-Chloroanthraquinone (9.0 g., 0.0372 mole) and formamide (90 ml.) were refluxed for 8 hours.

The reaction mixture was poured into cold water. The precipitated yellow solid was collected, washed with hot water several times and dried. Crystallization from benzene gave yellow needles (9.3 g., 92%) of N,N'-diformyl-9,10-diamino-2-chloroanthracene, m.p.  $> 360^{\circ}$  (Found: C, 64.14; H, 3.90; N, 8.41%.  $C_{16}H_{11}ClN_2O_2$ . requires: C, 64.43; H, 3.69; N, 9.39%); mass spectrum m/e 301(301), 300(17), 299(10), 298(50)( $M^+$ ), 271(4), 269(5), 264(2), 243(10), 242(9), 241(27), 240(5), 207(2), 205(5), 190(2), 177(3), 163(6), 129(6), 121(4), 102(4), 77(5), 76(5), 58(50), 43(100%), ...etc.;  $\nu_{max}$ . 3200-3125(M), 3000-2900(W), 1645(S), 1520(M), 1480(S), 1435(M), 1420(W), 1380(S), 1335(W), 1180(S), 1160(M), 1080(M), 950(W), 910(W), 875(M), 865(M), 800(M), 780(S), 745(M)  $cm^{-1}$ .

No unreacted starting material was recovered.

2. N,N'-Diformyl-9,10-diamino-2-chloroanthracene (9.0 g., 0.0302 mole) and formamide (100 ml.) were refluxed for 16 hours.

The reaction mixture was poured into cold water and the precipitate was collected, dried, and extracted with benzene (3 x 100 ml.) to give extract (A) and solid (B).

Thin layer chromatography (Silica gel/benzene) of the extract (A) showed unchanged starting material together with two unidentified materials. Column chromatography (Florisil/benzene) did not give enough material for identification.

Thin layer chromatography (Silica gel/benzene) of solid

(B)(8.8 g., 97.8%) showed unchanged starting material together with two unidentified materials (same <sup>as</sup> those spots <sup>which</sup> appeared in the t.l.c. of the extract A). The mass spectrum of the crude solid (B) showed peaks at m/e 255 and m/e 212 which were not observed in the spectrum of the pure starting material; these were thought to be due to N-formyl-10-amino-2-chloroanthracene and 2-chloroanthracene respectively. Several attempts to isolate these two compounds failed because of their low amounts.

3. N,N'-Di-formyl-9,10-diamino-2-chloroanthracene (9.0 g., 0.0302 mole), formic acid (50 ml.) and formamide (50 ml.) were refluxed for 9 hours.

The experiment was worked-up as in experiment (2). Unchanged starting material was recovered (8.5 g., 94%), contaminated with traces of two new compounds (<sup>the</sup> same two spots <sup>were</sup> which observed in the previous experiment). These could not be isolated.

ANTHRAQUINONE .

(1.) Anthraquinone (10 g., 0.0481 mole) and formamide (100 ml.) were stirred under reflux for 4 hours.

The reaction mixture was allowed to cool to room temperature and then filtered. The crude solid (11.9 g.) was washed with hot water several times, acetone (5 x 25 ml.) and then dried (100°) to give N,N'-diformyl-9,10-diaminoanthracene as a yellow amorphous powder (11.3 g., 89%) which was crystallized from benzene to give yellow needles (11.2 g., 88%) of pure N,N'-diformyl-9,10-diaminoanthracene, m.p.  $\rangle 360^{\circ}$  (Lit.<sup>56</sup>, 439°) (Found: C, 72.20; H, 4.63; N, 10.72%.  $C_{16}H_{14}N_2O_4$  requires: C, 72.72; H, 4.55; N, 10.61%); mass spectrum m/e 264( $M^+$ ) (3), 235(4), 206(6), 184(10), 167(11), 58(98), 43(100%), 28(82), 18(71), ...etc.;  $\nu_{\max}$ . 3215-3100(M), 2900(W, broad), 1648(S), 1525(M), 1500(S), 1435(W), 1385(S), 1365(M), 1270(M), 1190(S), 1160(M), 900(M), 850(M), 755(M), 730(M)  $cm^{-1}$ .

(2.) N,N'-Diformyl-9,10-diaminoanthracene (5.28 g., 0.02 mole), ammonium formate (6.3 g., 0.1 mole) and formamide (100 ml.) were refluxed for 3 hours.

The reaction mixture was diluted with water. The yellow precipitate was collected, dried and chromatographed (benzene/alumina) to give two fractions.

Fraction (I) gave, on evaporation, yellow solid which was sublimed to give yellow needles (1.1 g., 23%) of N-formyl-9-amino-10-hydroxyanthracene, m.p. 282-283.5° (Found: C, ;

H, ; N, %.  $C_{15}H_{11}NO_2$ . requires: C, 75.95; H, 4.64; N, 5.91%); mass spectrum  $m/e$  237 ( $M^+$ )(12), 236(24), 235(100%), 221(18), 210(24), 209(99), 208(72), 207(54), 206(60), 194(12), 193(11), 192(10), 185(17), 180(54), 152(21), ...etc. ;  $\nu_{max}$ . 3300-3100(M), 3020(W), 2950(W), 2860(M), 1650(S), 1575(W), 1515(S), 1440(W), 1415(W), 1375(S), 1290(W), 1275(W), 1215(S), 1175(M), 1015(W), 930(M), 875(S), 835(M), 750(S)  $cm^{-1}$ .etc.

Fraction (II) provided yellow needles (3.91 g., 74%) of unchanged starting material, m.p.  $> 360^\circ$ ; the mass spectrum was identical with that of the starting material.

#### THE REACTION OF N-FORMYL-9-AMINO-10-HYDROXYANTHRACENE WITH HYDROGEN PEROXIDE:

This was done by a modification of a literature method<sup>82</sup>. A solution of  $H_2O_2$  (6 ml.; 30%) and NaOH (100 mg., 2.5 m.mol.) in water (100 ml.) was added dropwise to a stirred solution of 10-hydroxy-N-formyl-9-aminoanthracene (237 mg., 1 m.mol.) in hot ethanol (100 ml.). After 3 hours more  $H_2O_2$  (6 ml.; 30%) was added. After a further 12 hours the solution was diluted with water (100 ml.) and the yellow precipitate was collected.

The crude product (159 mg.) was chromatographed (Florisil/benzene) to give two fractions.

Fraction (I) was evaporated. Crystallization from ethanol-benzene (3:1) gave yellow needles (78 mg., 37.5%) of anthraquinone, m.p.  $287^\circ$  (Lit.<sup>78</sup>,  $286^\circ$ );  $R_f$  and mass spectrum were identical with those of an authentic sample.



Fraction (II) provided yellow needles (57 mg., 24%) of unchanged starting material, m.p.  $283^{\circ}$ ;  $R_f$  and mass spectrum were identical with those of the pure starting material.

#### ANTHRONE.

Anthrone (9.7 g., 0.05 mole) and formamide (100 ml.) were refluxed for 8 hours.

The reaction mixture was poured into water. The yellow precipitate was collected (11.6 g.) and washed well with water and acetone (50 ml.). Chromatography on alumina (benzene) gave two fractions.

Fraction (I) was evaporated. Sublimation of the solid gave yellow needles (10.27 g., 87%) of N-formyl-9-amino-10-hydroxy-anthracene, m.p.  $282-283.5^{\circ}$ ; the mass spectrum and i.r. spectrum were identical with those of the previous sample of N-formyl-9-amino-10-hydroxyanthracene.

Fraction (II) (485 mg., 5%) was found (t.l.c.) to contain mainly unchanged starting material together with a trace of N-formyl-9-amino-10-hydroxyanthracene, m.p.  $151^{\circ}$ ; the mass spectrum and i.r. spectrum were similar to those of the pure starting material.

1,4-BENZOQUINONE.

1,4-Benzoquinone (2.16 g., 0.02 mole) and formamide (50 ml.) were refluxed for one hour.

The cold reaction mixture was filtered and the black solid was extracted with warm ethanol. The ethanol extract was evaporated to give an oily black material which was diluted with warm acetone (100 ml.) and allowed to cool. The precipitate was collected and sublimed to give yellow prisms (0.3 g., 13.6%) of hydroquinone, m.p.  $169.5^{\circ}$  (Lit.<sup>78</sup>,  $170^{\circ}$ ); mass spectrum  $m/e$  110( $M^{+}$ )(100%), 94(30), 81(40), 77(50), 59(70), 58(80),...etc.

1,4-NAPHTHOQUINONE.

1,4-Naphthoquinone (3.16 g., 0.02 mole) and formamide (50 ml.) were refluxed for two hours.

The reaction mixture was filtered to give a black crude solid (A) and solution (B).

The crude solid (A) was extracted with hot ethanol (5 x 50 ml.) to give extract (C) and a black amorphous powder (D).

Mass spectrum of (D)(2 g.) showed a spectrum identical with that of an authentic sample of anthraquinone. Extraction with ethanol or benzene failed to isolate any anthraquinone. Powder (D) looked like charcoal.

The extract (C) on cooling gave a greenish-yellow precipitate. Filtration gave crude solid (E) and solution (G).

Solid (E) was washed well with water and acetone and

then dried ( $100^{\circ}$ ) to give N,N'-diformyl-9,10-diaminoanthracene as a yellow amorphous powder (0.75 g., 28%), m.p.  $> 360^{\circ}$ ; the mass spectrum and i.r. spectrum were identical with those of the previous sample of N,N'-diformyl-9,10-diaminoanthracene.

The solution (G) was evaporated to give a yellow solid (0.045 g., 2%), m.p.  $> 300^{\circ}$ , which was thought to be N-formyl-9-aminoanthracene; mass spectrum m/e 221( $M^{+}$ ). This was not purified.

The solution (B) was diluted with water. No precipitate was obtained. The solution was discarded.

#### ATTEMPTED PREPARATION OF N-FORMYL-9-AMINOANTHRACENE.

9-Aminoanthracene-HCl (4.58 g., 0.02 mole), formic acid (25 ml.) and formamide (75 ml.) were refluxed for 16 hours.

The reaction mixture was poured into water. The yellow precipitate was collected (2.25 g.) and washed well with hot water and acetone (30 ml.). The crude solid was extracted with warm benzene (2 x 100 ml.). Thin layer chromatography (Florisil/benzene) of the benzene extract showed mainly three components. Column chromatography on Florisil (benzene) gave two fractions.

Fraction (I) was evaporated to give a mixture of two unidentified materials (0.7 g.). These were thought to be anthracene [same  $R_f$ ; mass spectrum m/e 178( $M^{+}$ )] and X,X'-dichloroanthracene (mass spectrum m/e 246,  $M^{+}$ , 2 chlorine atoms isotopic abundance). This mixture was not separated into its constituents.

Fraction (II) gave, on evaporation, yellow solid. Sublimation of the solid gave yellow needles (645 mg., 27%) of N-formyl-9-amino-10-hydroxyanthracene, m.p. 282-283°; the mass spectrum and i.r. spectrum were identical with those of the previous sample of N-formyl-9-amino-10-hydroxyanthracene.

The commercial sample of 9-aminoanthracene-HCl was treated with 2N NaOH solution. Thin layer chromatography (Silica gel/benzene) showed the presence of, at least, four components. This mixture was not separated into its constituents.

The commercial sample of 9-aminoanthracene-HCl was extracted with hot benzene (4 x 25 ml.) and the extract was chromatographed (Florisil/benzene) to give only one fraction which was evaporated and crystallized from benzene to give pure 9,10-dichloroanthracene (10.5%) as yellow needles, m.p. 210-210.5° (Lit.<sup>78</sup>, 210°); mass spectrum m/e 251(3), 250(63), 249(12), 248(63), 247(17)(M<sup>+</sup>,<sup>12</sup>), 246(100%)(M<sup>+</sup>,<sup>35</sup>Cl), 211(4)(M<sup>+</sup>-Cl), 176(68)(M<sup>+</sup>-2Cl), ...etc.

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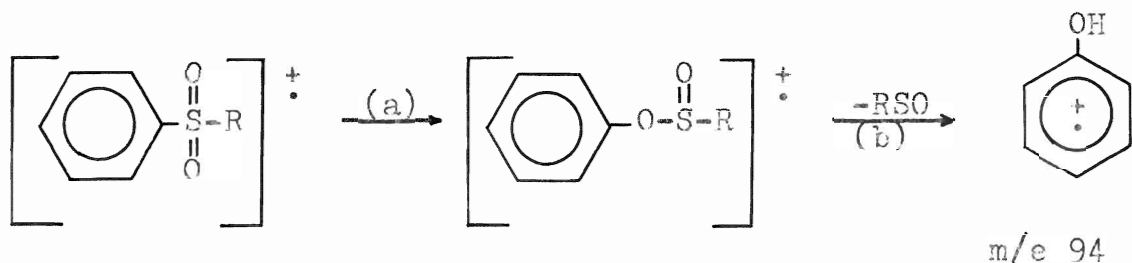


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A P P E N D I X

APPENDIX  
OBSERVATIONS AND COMMENT ON THE MASS  
SPECTRA OF THE DIARYL  
SULFONES

For a number of alkyl phenyl sulfones, Mayerson and McCollum<sup>83</sup> have reported a process leading to the ion  $(C_6H_5-OH)^{+\bullet}$  (m/e 94). This involves 1,2-phenyl migration from sulfur to oxygen (step b)(equation 1).



Diaryl sulfones with different aryl substituents can undergo migration of either aryl groups. An aryl group better able to function as an electron donor should preferentially migrate. Indeed, Meyerson and Co-workers<sup>84</sup> have demonstrated that migratory aptitude apparently increases with increasing substitution of the phenyl group by electron-donating methyl groups, although some complications due to further decomposition of the fragment ions arise in the interpretation of their data<sup>84</sup>.

The migration process can be presented in a simple diagram similar to that which has appeared in the literature (Diagram I). The relative abundances of the ions  $(C_6H_5O^{\bullet} \text{ or } ^+)$  (or  $R-C_6H_4-SO^{\bullet} \text{ or } ^+$ ) and  $(C_6H_5SO^{\bullet} \text{ or } ^+)$  (or  $R-C_6H_4-O^{\bullet} \text{ or } ^+$ ) reflect the abilities of the phenyl and R-phenyl groups to

migrate respectively. One would expect, therefore, that the R-phenyl group would migrate (Route a) preferentially in the order  $R = \text{EtO-} > \text{NH}_2 > \text{NO}_2$  and therefore the relative abundances of the ions (A)(Diagram I) will be in the series:

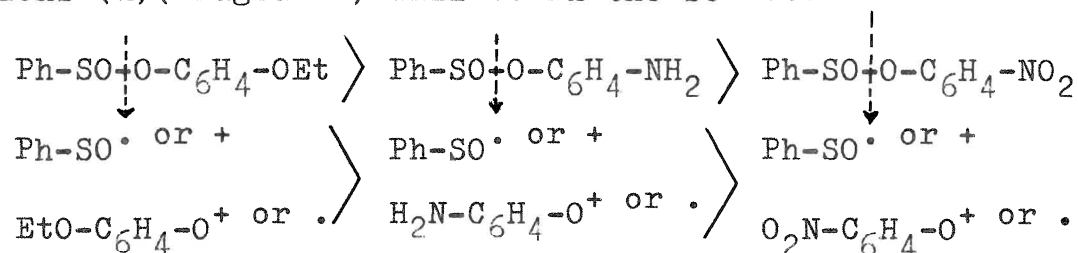
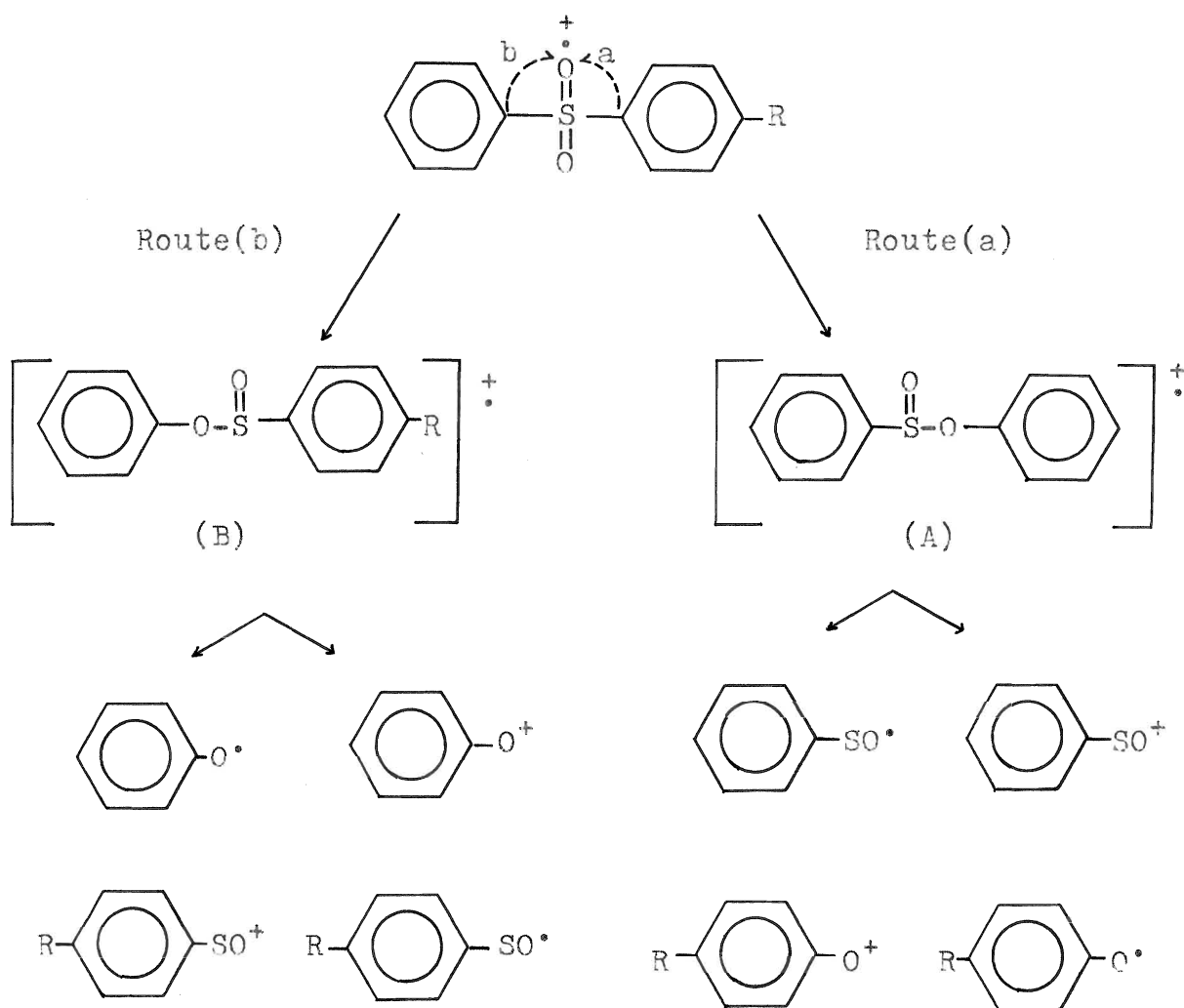


DIAGRAM (I)



In fact, the relative abundances of the ions  $R-C_6H_4-O^\bullet$  or  $+$  are found to be in the order  $H_2N-C_6H_4-O \rangle EtO-C_6H_4-O \rangle O_2N-C_6H_4-O$  (As shown in Table I). The lower abundance of  $EtO-C_6H_4-O$  than of  $H_2N-C_6H_4-O$  can be explained in terms of the easier breakdown of the ethoxy-group ( $-Me^\bullet$  and  $CH_2=CH_2$ ) than the amino-group.

But, surprisingly, the trend is reversed for the ion  $Ph-SO^\bullet$  or  $+$

$PhSO$  when  $R=OEt$   $\left\langle \begin{array}{l} PhSO \\ \text{when } R=NH_2 \end{array} \right\langle \begin{array}{l} PhSO \\ \text{when } R=NO_2 \end{array}$ . This is in disagreement

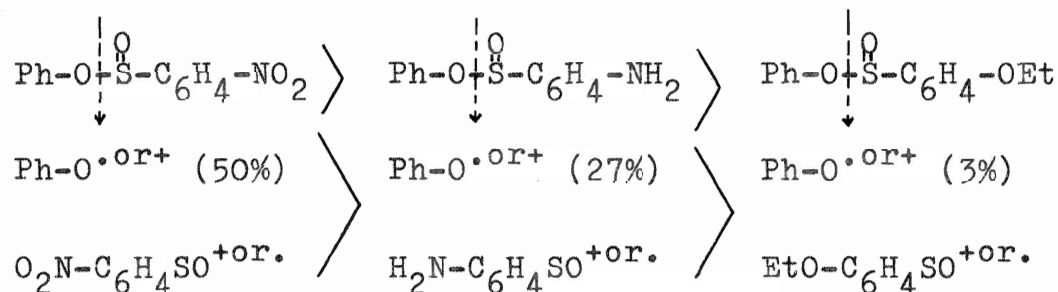
with the present proposition and raises a doubt about the proposed transition state (explained in the literature<sup>69</sup> in terms of the electron deficiency being largely localized in a non-bonding oxygen orbital (  $Ar-\overset{\overset{O^\bullet}{\parallel}}{S}-Ar'$  ) so that the better

TABLE (I)

ION		$R=NO_2$	$R=NH_2$	$R=OEt$
Route (b)	$Ph-O^\bullet$ or $+$	m/e93,50%	m/e93,27%	m/e93,3%
	$R-C_6H_4SO^{+or.}$	m/e170,38%	m/e140,43%	m/e169,4%
Route (a)	$PhSO^{+or.}$	m/e125,75%	m/e125,11%	m/e125,8%
	$R-C_6H_4O^\bullet$ or $+$	m/e138,0.2%	m/e108,98%	m/e137,5%

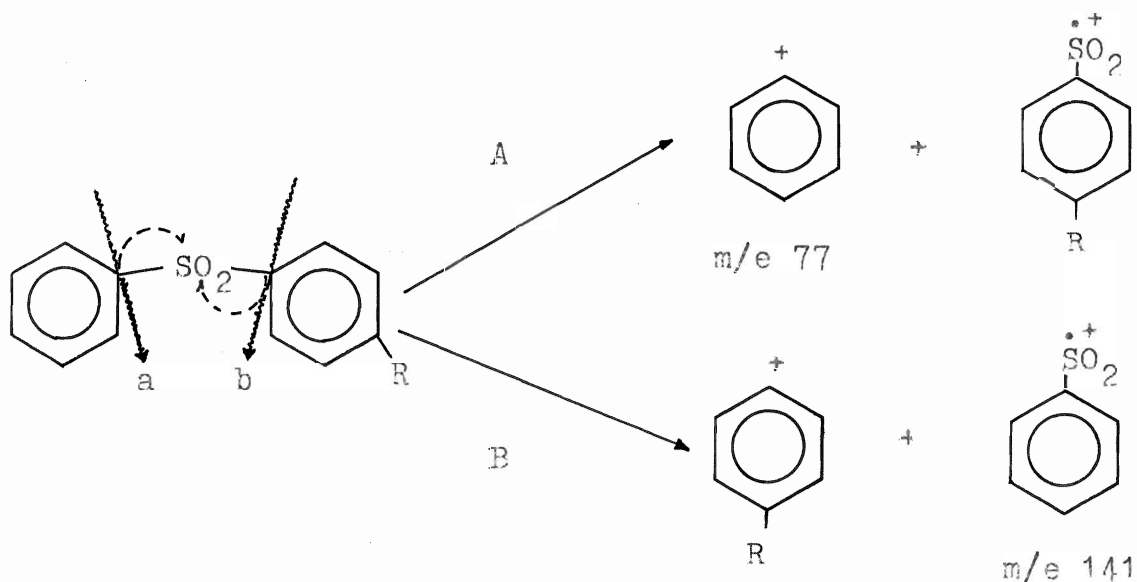
electron donor aryl group should preferentially migrate).

On the other hand, a perfect trend of abundances is found in route (b) (Diagram I) which is completely consistent with the present proposition. That is, the ion B (Diagram I) (or, otherwise the phenoxy ion derived from B) is more readily formed as the ability of the aryl group to function as an electron donor increases:



A second process which is rather interesting and apparently has not attracted attention in the current literature is that of breakage at either side of the sulfone group. It seems that the ability of the aryl group to function as an electron attractor (or electron donor) is the limiting-factor in this process (Diagram II). The results which are given (Table, II) suggest that the formation of the ion  $\text{C}_6\text{H}_5^+$  (or  $\text{R}-\text{C}_6\text{H}_4-\text{SO}_2^{\cdot+}$ ) (Route A) is favored when the R-group is better able to function as an electron attractor  $\left[ \text{R} = \text{NO}_2 \text{ (m/e77, 100\%)} \rangle \text{NH}_2 \text{ (m/e77, 79\%)} \rangle \text{OEt (m/e77, 8\%)} \right]$ .

On the other hand, the formation of the ion  $\text{C}_6\text{H}_5\text{SO}_2^{\cdot}$  (or  $\text{R}-\text{C}_6\text{H}_4^+$ ) (Route B) is favored when the R-group is better able to function as an electron donor  $\left[ \text{m/e 141} = 16\% \text{ (R=NO}_2\text{)} \langle 17\% \text{ (R=NH}_2\text{)} \langle 55\% \text{ (R=OEt)} \right]$ .

DIAGRAM (II)TABLE (II)

Route	ION	R=NO <sub>2</sub>	R=NH <sub>2</sub>	R=OEt
A	$\text{C}_6\text{H}_5^+$	$m/e$ 77, 100%	$m/e$ 77, 79%	$m/e$ 77, 8%
	$\text{R-C}_6\text{H}_4\text{-SO}_2^\bullet$	$m/e$ 186, 0.3%	$m/e$ 156, 18%	$m/e$ 185, 2%
B	$\text{C}_6\text{H}_5\text{-SO}_2^\bullet$	$m/e$ 141, 16%	$m/e$ 141, 17%	$m/e$ 141, 55%
	$\text{R-C}_6\text{H}_4^+$	$m/e$ 122, 0.1%	$m/e$ 92, 61%	$m/e$ 121, 3%

Again, probably due to the ready breakdown of the ethoxy-group, the relative abundances of the ions  $\text{R-C}_6\text{H}_4^+$  are observed in the order  $\text{R} = \text{NO}_2 < \text{EtO} < \text{NH}_2$ . These however are consistent

with the proposition.

Finally, loss of  $\text{SO}_2$  molecule in a one-step process to give  $(\text{M}-\text{SO}_2)^{\cdot+}$  is also apparent in the spectra of the corresponding sulfones (Diagram III). However, this process seems to be independent of the nature of R-group, as expected. The data are given in Table (III).

DIAGRAM (III)

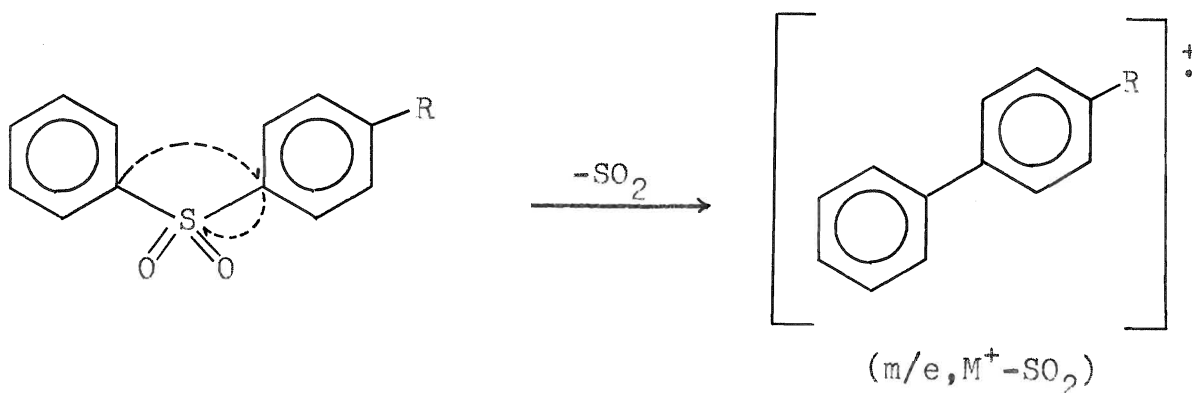


TABLE (III)

ION	R = $\text{NO}_2$	R = $\text{NH}_2$	R = $\text{OEt}$
$(\text{M} - \text{SO}_2^{\cdot+})$	m/e 199, 0.3 %	m/e 169, 16 %	m/e 198, 0.3 %



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