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PART I

THE PREPARATION OF 1,8-DIMETHYLNAPHTHALENE

PART II

GRIGNARD REACTIONS ON NAPHTHALIC ANHYDRIDE

by

Glenn W. Mansell

A Thesis presented to the Committee on Post-Graduate Studies
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INDEX

PART I

THE PREPARATION OF 1,8-DIMETHYLNAPHTHALENE

	Page
GENERAL SUMMARY.....	1
INTRODUCTION.....	2
A Reported Preparations of 1,8-Dimethylnaphthalene.....	4
B Preparations and Properties of 1,8-Dihalonaphthalenes..	8
1. Nitration of 1-naphthylamine.....	9
2. Nitration of 1-nitronaphthalene.....	11
3. Chlorination of 1-nitronaphthalene.....	17
4. Reactions of sulphonic acids.....	21
EXPERIMENTAL WORK:	
A Preparation of 8-chloro-1-nitronaphthalene.....	25
B Preparation of 8-chloro-1-naphthylamine.....	26
C Preparation of 1-bromo-8-chloronaphthalene.....	27
D Preparation of 1,8-dichloronaphthalene.....	29
E Attempted preparations of 1,8-dimethylnaphthalene.....	30
F Chlorination of 1-nitronaphthalene.....	35
G Bromination of 1-nitronaphthalene.....	41
H Nitration of 1-nitronaphthalene.....	42
DISCUSSION OF RESULTS.	
A Mechanisms for the chlorination of 1-nitronaphthalene..	45
B Chlorination of 1-nitronaphthalene.....	52
C Bromination of 1-nitronaphthalene.....	53
D Nitration of 1-nitronaphthalene.....	54
E Preparation of 1,8-dihalonaphthalenes.....	55
F Attempted preparation of 1,8-dimethylnaphthalene.....	57

Index (Continued).

Page

X-RAY POWDER PHOTOGRAPHS.....	60
BIBLIOGRAPHY.....	67

PART II

GRIGNARD REACTIONS ON NAPHTHALIC ANHYDRIDE

GENERAL SUMMARY.....	71
INTRODUCTION.....	73
EXPERIMENTAL WORK.....	75
DISCUSSION.....	77
BIBLIOGRAPHY.....	78

PART I

THE PREPARATION OF 1,8-DIMETHYLNAPHTHALENE.

GENERAL SUMMARY

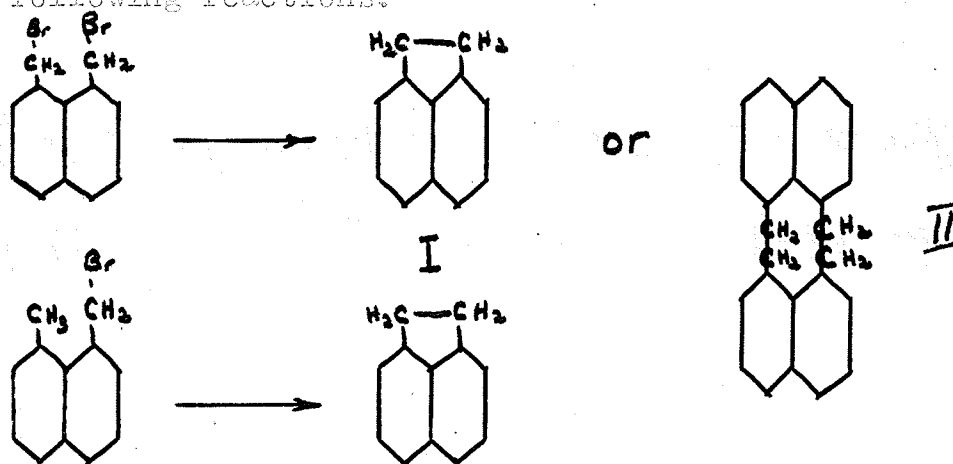
The preparation of 1,8-dimethylnaphthalene from compounds having a naphthalene nucleus presents an interesting problem, insofar as only one such preparation has been reported. The method used (74) was not suitable for a convenient preparation, while the description of the compound so produced is quite unlike that for the compound prepared from benzene derivatives by building up the second aromatic ring. Furthermore, the workers (10, 53) who have prepared 1,8-dimethylnaphthalene from benzene compounds give different melting points for the picrate derivative.

Another report (32) has indicated that 1,8-dimethylnaphthalene was obtained as a byproduct in the preparation of 8-bromo-1-methylnaphthalene from 8-bromo-1-iodonaphthalene through the Grignard reaction with one mole of magnesium. The monomethyl derivative was required in connection with a larger synthesis, and apparently no effort was made to characterize the reported 1,8-dimethylnaphthalene.

The preparation of 1,8-dimethylnaphthalene by the Grignard reaction seemed to be promising, as many methods have been reported for the preparation of the necessary 1,8-dihalonaphthalenes. It was further proposed that by bromination of 1,8-dimethylnaphthalene under appropriate conditions, the methyl groups might be attacked, without nuclear substitution,

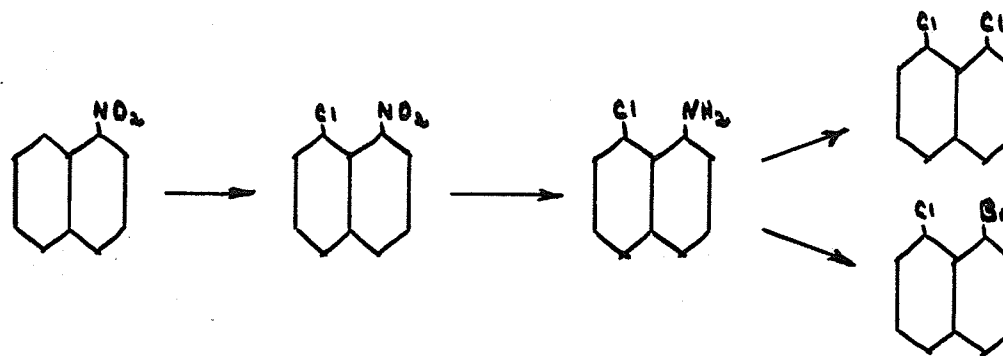
to give the corresponding methyl-bromomethyl, or (bis-bromo-methyl) naphthalene. The use of N-bromosuccinimide gave this result with 1- and 2-methylnaphthalenes, and with 2,6- and 2,7-dimethylnaphthalenes, according to Buu-Hoi and Lecocq (22).

These compounds in turn, on dehalogenation, might lead to the following reactions:



The preparation of the naphthalene dimer II would be analogous to the preparation of perylene from 1,8-di-iodo-naphthalene by Scholl, Seer, and Weitzenbock (66), while the preparation of acenaphthene I from naphthalene by this method would present an interesting alternative to the synthesis of acenaphthene from naphthalene as outlined by Schonberg, Moubasher, and Mostafa (65).

In the present work, considerable difficulty has been encountered in attempts to prepare the starting materials required for the preparation of the desired 1,8-dihalonaphthalenes. The following reactions have been successfully carried out:



However, the preparation of the Grignard reagents from 1,8-dichloronaphthalene and 1-bromo-8-chloronaphthalene by reaction with magnesium in anhydrous ether proceeded only very slowly, giving crystalline reagents, and without the complete reaction of two moles of magnesium. Methylation with methyl iodide gave only the starting material, while methylation with methyl sulphate gave only oils, from which no crystalline product could be isolated.

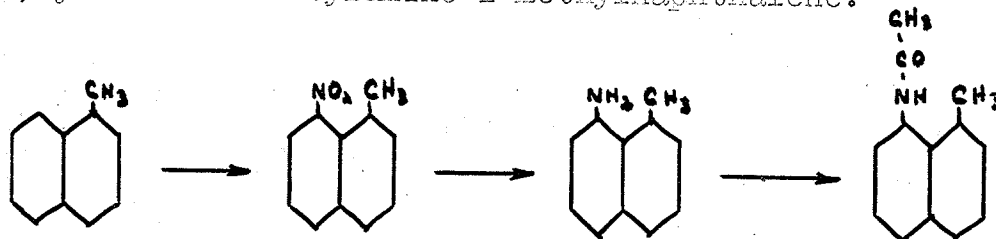
X-ray powder photographs have been taken of a number of the crystalline naphthalene compounds used in this investigation.

INTRODUCTION.

A Reported Preparations of 1,8-Dimethylnaphthalene.

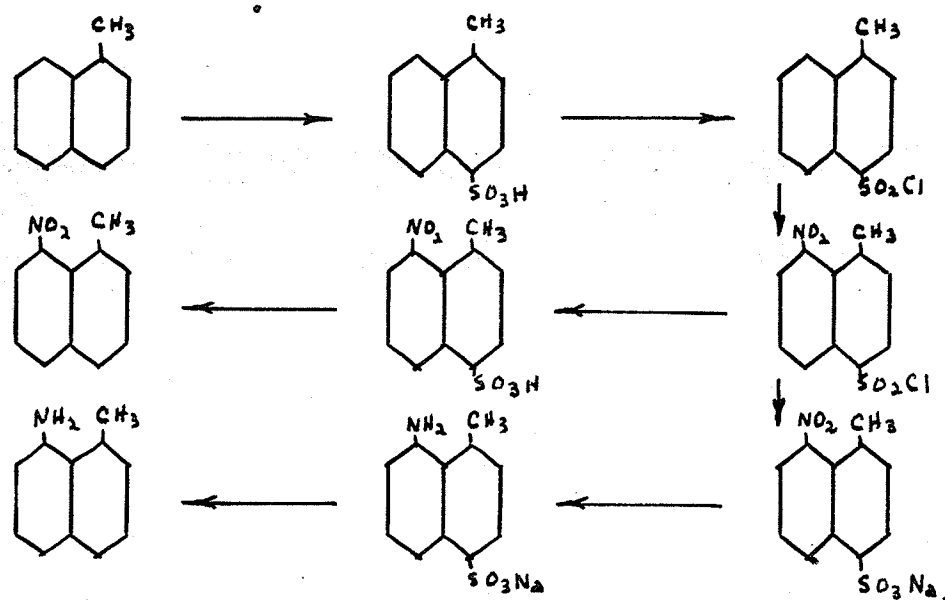
(1) The first preparation of 1,8-dimethylnaphthalene was reported by Vesely and Stursa (74) in 1931, as a result of work carried out by Steiger (68), and by Vesely, Stursa, Olejnicek, and Rein (75). Though the method of preparation is not suitable for a convenient synthesis, it is of historical interest as the first synthesis of this product. The methods of synthesis were as follows:

1-Methylnaphthalene, when nitrated with fuming nitric acid in glacial acetic acid, gave principally the 4-nitro-isomer, with small amounts of other isomers, including 1-methyl-8-nitronaphthalene. This latter, on reduction with stannous chloride and hydrochloric acid, followed by acetylation, yielded 8-acetylamino-1-methylnaphthalene.



1-Methylnaphthalene, treated with cold chlorosulphonic acid, followed by neutralization with potassium carbonate and steam distillation, gave 1-methyl-4-naphthalenesulphonic acid, which on treatment with phosphorus pentachloride, gave the sulphonyl chloride. Nitration with concentrated nitric acid gave a mixture of the 5- and 8-nitro isomers. The latter, on treatment with sodium sulphite solution and then with sulphuric acid, gave 1-methyl-8-nitronaphthalene.

On heating 1-methyl-8-nitro-4-naphthalenesulphonyl chloride with sodium hydroxide, followed by reduction with iron, 8-amino-1-methyl-4-naphthalenesulphonic acid was obtained. Elimination of the sulphonic acid group with sodium amalgam gave 1-methyl-8-naphthylamine.



1-Methyl-8-nitronaphthalene was also produced from 1-methyl-5-nitro-4-naphthalenesulphonyl chloride by elimination of the sulphonyl chloride group and reduction to 1-methyl-5-naphthylamine. The acetyl derivative, on nitration, gave a mixture of the 6- and 8-nitro derivatives. Separation of the 5-acetylamino-1-methyl-8-nitronaphthalene, followed by saponification and elimination of the amino group, gave 1-methyl-8-nitronaphthalene.

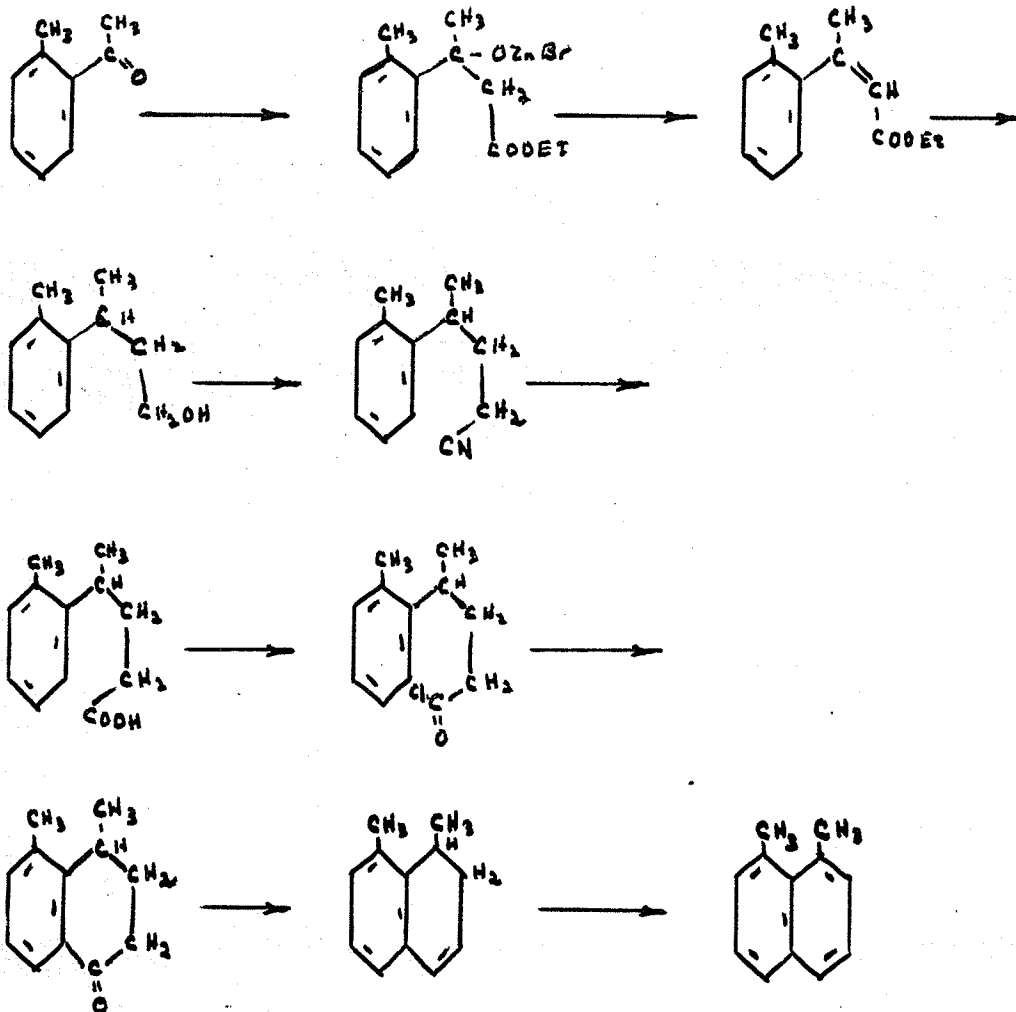
From 1-methyl-8-naphthylamine, 1-methyl-8-bromonaphthalene was prepared by the Sandmeyer reaction. This was mixed with a solution of methyl magnesium iodide in dry ether, and methyl sulphate was added. The resulting Grignard complex was decomposed, and the 1,8-dimethylnaphthalene was obtained.

by steam distillation as an oil which would not solidify at -20° . The picrate derivative melted at $143-144^{\circ}$. The yield from 1.7 gm. of 8-bromo-1-methylnaphthalene was 0.4 gm. of 1,8-dimethylnaphthalene.

(2) A second method of synthesis of 1,8-dimethylnaphthalene is given by Linstead and his co-workers (53). These workers used as a starting material o-methyl-acetophenone, which can be prepared by the method of Campaigne and Reid (23) from o-tolyl magnesium bromide; from o-toluic acid by the method of Kadesch (50); or from benzyl magnesium chloride by the method of Newman and Booth.(60).

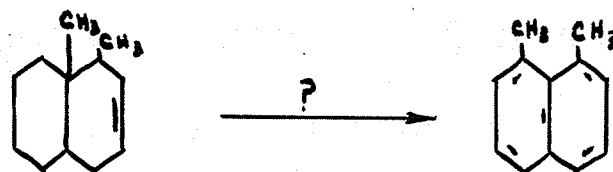
o-Methyl acetophenone was condensed with ethylbromacetate and zinc in benzene, and the product was distilled with a little iodine. The β -o-tolyl crotonic ester obtained was reduced with sodium in alcohol, and the γ -o-tolyl butanol was isolated by distillation, first with steam, then under reduced pressure. This was converted through the bromide and nitrile in the usual way into γ -o-tolyl valeric acid. The chloride of this acid was cyclized by means of aluminum chloride in carbon disulphide to 4,5-dimethyl-1-tetralone. The ketone was reduced by means of sodium in alcohol, the solvent was removed with steam, and the residue was isolated by means of ether. After distillation with a crystal of iodine, 1,8-dimethyl-1,2-dihydronaphthalene was obtained. This was dehydrogenated with selenium for twelve hours at 300° . The 1,8-dimethylnaphthalene solidified after distillation (B.P.

140°/18 mm.) and formed white leaflets from dilute alcohol, melting at 63°. The orange-yellow picrate melted at 148°, while the orange-yellow styphnate melted at 160°.



(3) This method of preparation has been used recently by Bailey, Bryant, Hancock, Morrell, and Smith (10) in connection with their study of the ten dimethyl isomers of naphthalene. These workers report the following data for 1,8-dimethylnaphthalene: M.P. 62.5°, B.P. 270°; Picrate M.P. 156°; Styphnate M.P. 161°; Trinitrobenzoate M.P. 167°.

(4) Elliott and Linstead (27) have described the dehydrogenation of 1,9-dimethyl- $\Delta^{2,3}$ -octalin over palladised asbestos at 335° for four hours, which yielded a liquid. The picrate derivative of this liquid gave an analysis agreeing with that for a picrate of dimethylnaphthalene. It is suggested by these authors that the picrates of 1,8- and 1,2-dimethylnaphthalene were probably present.



B Preparations and Properties of 1,8-Dihalonaphthalenes.

A survey of the literature indicates a considerable variety of compounds which may be used as intermediates for the preparation of 1,8-dimethylnaphthalene through Grignard reactions on 1,8-dihalonaphthalenes. These intermediates, to be of use, must have substituents only in the 1 and 8 positions, and must give good yields of the desired 1,8-dihalonaphthalenes. Furthermore, they must be capable of preparation from compounds available commercially.

Four types of reactions involving simple materials may lead to intermediates suitable for conversion into 1,8-dihalonaphthalenes. These are:

- (1) Nitration of 1-naphthylamine.

- (2) Nitration of 1-nitronaphthalene.
- (3) Chlorination of 1-nitronaphthalene.
- (4) Reactions involving sulphonic acids.

The following review of the literature shows how each of these reactions may lead to the desired products.

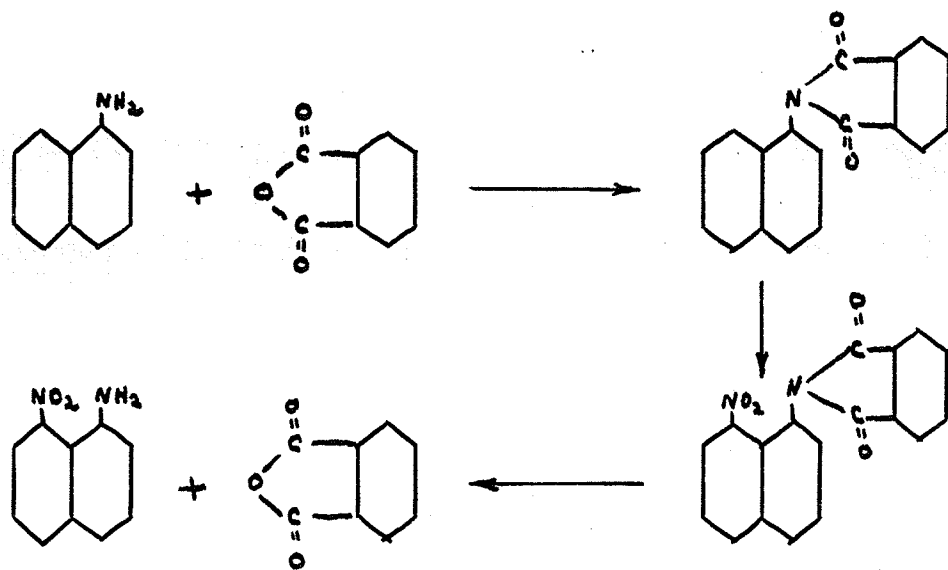
(1)a. Nitration of 1-naphthylamine.

The preparation of 8-nitro-1-naphthylamine by nitration of 1-naphthylamine was first reported by Meldola and Streatfield (56), who used a method developed by Noelting and Collin (61). This consisted in the nitration of 1-naphthylamine in a strong sulphuric acid solution, yielding a mixture of 4-, 5-, and 8-nitro-1-naphthylamines, the 8-nitro isomer being much more soluble in dilute sulphuric acid than the others. The yield of this isomer was 6-8% by weight of the 1-naphthylamine used.

Morgan and Micklethwait (59) obtained the same yield, while Morgan and Jones (58) made some modifications which increased the yield of the 8-nitro isomer to 18.5% of theory, along with a 72.5% yield of the 5-nitro isomer.

Hodgson and Crook (43) have introduced a different technique which greatly increases the yield of the 8-nitro isomer, and avoids the tar formation which accounts for the low yields of the older method. They first reacted 1-naphthylamine with phthalic anhydride in boiling tetralin, to obtain phthalic-1-naphthylimide. This, on nitration, gave the 8-, 5-, and 4-nitro isomers in the ratio of 60:28:5.

Hydrolysis of the nitrated mixture with aqueous ammonia at 130° in an autoclave gave a mixture of nitro-naphthylamines, from which the 8-nitro isomer could be extracted with 10% sulphuric acid solution. The yield of 8-nitro-1-naphthylamine, based on the 1-naphthylamine used, was 33.8%.



Hodgson and Ratcliffe (45) used hydrolysis with ethanolic hydrazine hydrate to avoid the higher pressure and temperature, but this decreased the yield to 17.8%.

b. Reactions of 8-nitro-1-naphthylamine.

Meldola and Streatfield (56) first investigated the reactions of 8-nitro-1-naphthylamine. Diazotization and a Sandmeyer reaction with cuprous bromide gave 1-bromo-8-nitronaphthalene. This on reduction with zinc and acetic acid gave the corresponding amine, which, on diazotization and the Sandmeyer Reaction with cuprous bromide, gave 1,8-dibromo-

naphthalene.

Asaoka (6) reported the preparation of 1-chloro-8-nitronaphthalene from 1-naphthylamine, presumable through the nitronaphthylamine and a Sandmeyer reaction with cuprous chloride, though the original paper was not available for study.

Hodgson and Crook (44) prepared 1-iodo-8-nitronaphthalene by diazotization of the amine and treatment with potassium iodide, while Willstaedt and Scheiber (80) prepared 8-nitronaphthalene-1-diazoborofluoride by treatment of the diazotized amine with borofluoric acid. This compound exploded on heating, so that attempts to prepare the corresponding 8-nitro-1-fluoronaphthalene by thermal decomposition were unsuccessful. It was reported that 1,8-dinitronaphthalene was prepared by nitration of 1-nitronaphthalene with acid.

Freidlander and Willstaedt (36) gave an extensive survey of the oxidation reactions of 1,5- and 1,8-dinitronaphthalene with various reagents, and also reported the preparation of 1,8-dinitronaphthalene by nitration of 1-nitronaphthalene with concentrated nitric acid in fuming sulphuric acid.

(2)a. Nitration of 1-nitronaphthalene.

1,8-Dinitronaphthalene has been known since before 1873, when d'Aguiar (2) reported its melting point at 170°. Gassmann (39) made a study of its preparation from naphthalene by nitration with concentrated nitric acid in fuming sulphuric acid. A maximum yield of 67.9% was reported.

Freidlander (36) in 1899, reported that nitration of 1-nitronaphthalene gave a mixture of 1,5- and 1,8-dinitronaphthalene, which could be separated by the use of the proper amount of sulphuric acid in the nitric acid-sulphuric acid nitrating mixture. The 1,5- isomer crystallized out on cooling, while the 1,8- isomer remained in the acid solution.

Finzi (35) in 1925, used this method of separating the isomers, suggesting the use of a nitrating mixture of 88.63% sulphuric acid, 5.97% nitric acid, and 5.40% water. On heating to 90° and allowing to cool slowly, the 1,5- isomer could be filtered off at 50° , and the 1,8-dinitronaphthalene at 15° .

Lucius and Bruning (54) in 1910, had suggested the use of sulphites in solution to treat the mixed isomers. The 1,5- isomer was reduced and sulphonated, while the unattacked 1,8- isomer was separated by filtration. H.H. Hodgson and various co-workers have improved this method of selective reduction of the 1,5-dinitronaphthalene to 5-nitro-1-naphthylamine, which can then be separated from the unreduced 1,8-dinitronaphthalene by extraction with acid.

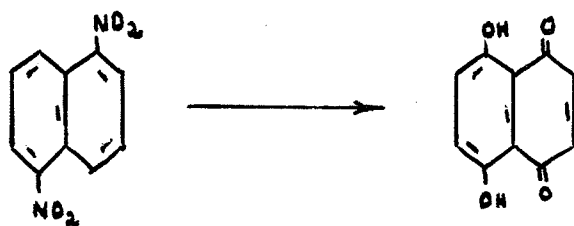
Hodgson and Walker (46) made an extensive study of the reduction of a mixture of 1,5- and 1,8-dinitronaphthalene with sodium monosulphide and sodium trisulphide in aqueous solutions at 65° and 90° , obtaining maximum yields of about 40% of 1,8-dinitronaphthalene, together with 12-14% of 5-nitro-1-naphthylamine.

Hodgson and Whitehurst (48) in 1945, made improvements in this experimental method, obtaining yields of 36% of the pure 1,8-dinitronaphthalene. These workers also showed by a quantitative nitration of 1-nitronaphthalene that, under the conditions used, the nitrated mixture consisted of 64% of the 1,8- isomer, and 36% of the 1,5-dinitronaphthalene.

Hodgson and Ward (47) in 1947, presented another modifi-

cation of this selective reduction method, carrying out the reduction with sodium sulphide and sodium bicarbonate in boiling methanol. Though the amount of reducing agent used had to be carefully regulated, the yield of 1,8-dinitronaphthalene obtained was 63% of the nitrated mixture, or 95-96% of the 1,8- isomer present in the mixture.

Gallotti and Galimberti (38) have suggested a separation of the mixture of isomers by selective oxidation of the 1,5- isomer to naphthazarin, using a mixture of sulphuric acid and oleum. This gave a recovery of 90% of the 1,8- isomer present in the mixture.



A different method of nitration has been suggested by Zakharov (81), which seems to avoid the separation of isomers. Nitration of naphthalene with nitrogen dioxide, in the presence of mercuric nitrate, gave yields of 65-90% of 1,8-dinitronaphthalene.

b. Reactions of 1,8-dinitronaphthalene.

Atterberg (8) in 1876, reported the preparation of 1,8-dichloronaphthalene by reacting molten 1,8-dinitronaphthalene with phosphorus pentachloride.

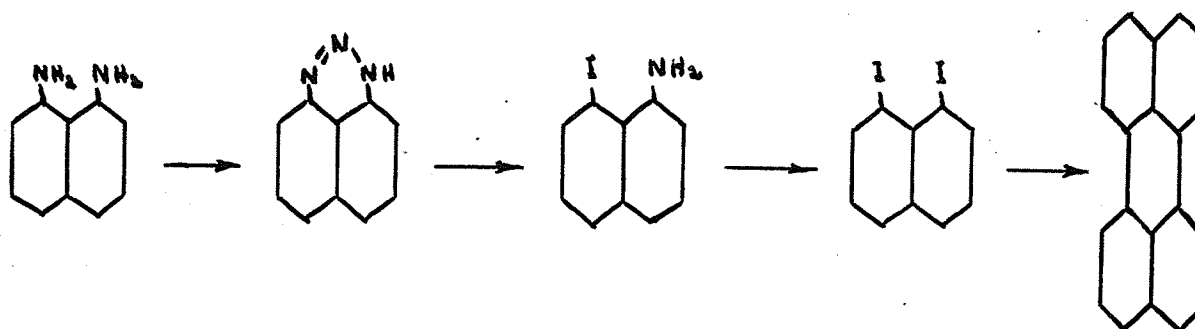
d'Aguiar (3) two years earlier, had described the red-

uction of 1,8-dinitronaphthalene to 1,8-naphthalenediamine. Meyer and Muller (57) used phosphorus iodide and water to obtain yields of 65-70% of the diamine from 1,8-dinitronaphthalene. More recently, a number of different methods have been used to accomplish the reduction. Vesely and Rein (73) reported a partial reduction to 8-nitro-1-naphthylamine with hydrogen and a platinum black catalyst. Vorozhtsov and Koslov (78) reported a 77% yield of the diamine by passing hydrogen sulphide and a weak stream of dry ammonia into a solution of 1,8-dinitronaphthalene in aniline at 160-165° for two to three hours, followed by distillation of the aniline, and crystallization from water. Strel'tsova and Zelinskii (70) reported quantitative reduction to the diamine in an ethanol solution, using purified electrolytic hydrogen and a platinum catalyst. Hodgson and Whitehurst (49) reported the use of iron powder, ferrous sulphate, and water as a reducing agent.

c. Reactions of 1,8-naphthalenediamine and its derivatives.

d'Aguiar (3) in 1874, first reported that the action of nitrous acid on 1,8-naphthalenediamine gives a diazo-amine. Scholl, Seer, and Weitzenbock (66) in 1910, converted this compound into 8-iodo-1-naphthylamine by the action of hydriodic acid and copper powder, in almost 100% yield. Diazotization of the amine, followed by treatment with potassium iodide, gave 1,8-di-iodonaphthalene, which in turn gave the

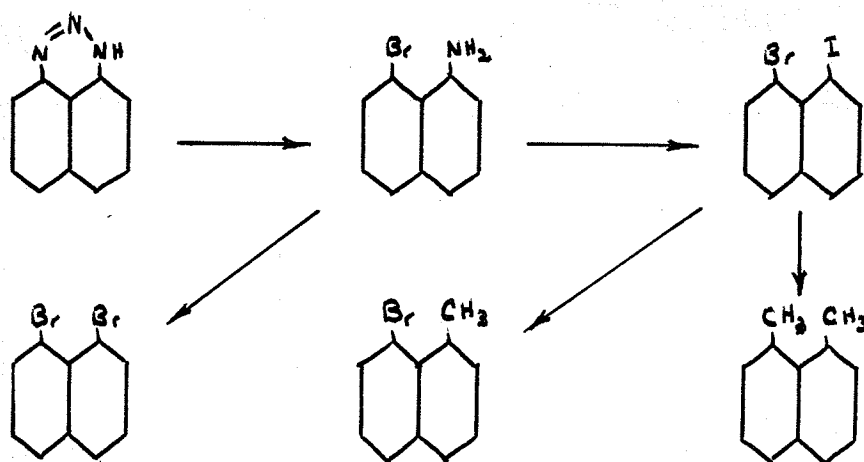
hydrocarbon perylene, on heating with copper powder at 120°.



Busch and Weber (21) attempted to prepare perylene by reduction of 1,8-di-iodonaphthalene and 1,8-dibromonaphthalene in methanolic potassium hydroxide with hydrazine hydrate and a palladium catalyst. Naphthalene, dihydronaphthalene, and tetralin were isolated, while the presence of perylene was indicated by the intense fluorescence of the products.

Feiser and Seligman (32), by reaction with hydrochloric acid and sodium nitrite, converted 1,8-naphthalenediamine into the diazo-imine, and thence into 8-bromo-1-naphthylamine on treatment with hydrobromic acid and copper. Diazotization of this amine, and reaction with potassium iodide, gave 8-bromo-1-iodonaphthalene. In the preparation of the Grignard reagent from this compound with one mole of magnesium, it was found that if the reaction was allowed to proceed slowly, the resulting Grignard reagent, on methylation with methyl iodide and methyl sulphate, gave 8-bromo-1-methylnaphthalene. When the Grignard reaction was allowed to proceed more rapidly, the product obtained after methylation contained 1,8-dimethylnaphthalene and unchanged 8-bromo-1-iodonaphthalene. Feiser and Seligman give no report of the characterization of the 1,8-dimethylnaphthalene so obtained.

Reaction of diazotized 8-bromo-1-naphthylamine with hydrobromic acid and cuprous bromide gave 1,8-dibromonaphthalene, which gave only a very slow reaction with magnesium to form a sparingly soluble Grignard reagent. Attempted formation of the Grignard reagent from 8-bromo-1-methylnaphthalene and magnesium also proceeded slowly, apparently because of the separation of colorless crystals of the reagent.



Erdmann (28) first reported the tetrazotization of 1,8-naphthalenediamine, which was followed by treatment with cuprous chloride to give 1,8-dichloronaphthalene. Hampson and Weissberger (41) have also used this method, while Hodgson and Whitehurst (49) tetrazotized the diamine in glacial acetic acid, and prepared 1,8-dichloro, 1,8-dibromo, and 1,8-di-iodonaphthalene by reactions with cuprous chloride in hydrochloric acid, cuprous bromide in hydrobromic acid, and potassium iodide in water, respectively.

(3) a. Chlorination of 1-nitronaphthalene.

The chlorination of 1-nitronaphthalene is far more complex than would be expected. While mono- and dichloro-nitronaphthalenes can be prepared under certain conditions by direct chlorination, other products are almost always present as well. The nitro group is frequently eliminated with the formation of naphthalene and polychloro-naphthalenes.

For the preparation of chloro-nitronaphthalenes, the variations of a method developed by Ullmann and Consonno (72) seem most satisfactory. These workers chlorinated fused 1-nitronaphthalene at 40-60° with one mole of chlorine, in the presence of ferric chloride. 8-Chloro-1-nitronaphthalene crystallized from the resulting oil on standing. Ferrero and Caflish (33) indicated the formation of 5- and 8-chloro-1-nitronaphthalene by this method. These authors used steam distillation to remove unreacted 1-nitronaphthalene, and suggested fractional crystallization from xylene or alcohol to separate the small amount of the 5-chloro-isomer from the 8-chloro-1-nitronaphthalene. Adams and Steele (1) obtained yields of 19.5% of 8-chloro-1-nitronaphthalene, while Feiser and Seligman increased the yield to 36.5%. Bayer (11) reported that exhaustive chlorination of 1-nitronaphthalene under these conditions gave 1-nitro-5,8-dichloronaphthalene.

Vorozhtsov and Koslov (77) chlorinated 1-nitronaphthalene at 60-70° in the presence of ferric chloride. Steam distillation and fractional crystallization from alcohol gave 5- and 8-chloro-1-nitronaphthalene, and also nitrogen free products, which included 1-chloronaphthalene and 1,4,5-

trichloronaphthalene. Nitrogen free products from the chlorination of 1-nitronaphthalene have also been reported by several other workers.

Atterberg (7) was among the first to study the action of gaseous chlorine on fused 1-nitronaphthalene. He found that one mole of chlorine was absorbed without the elimination of hydrogen chloride, forming an addition compound, a thick brown oil. Distillation of this oil resulted in the evolution of hydrogen chloride and reddish vapors. On redistillation and recrystallization, 1-chloronaphthalene, 1,5-dichloronaphthalene, 1,3,5-trichloronaphthalene, and a tetrachloronaphthalene melting at 194° , were obtained. This tetrachloronaphthalene is probably identical with the 1,2,3,4-tetrachloronaphthalene melting at 198° reported by Braun (18) and that melting at 196° reported by Turner and Wynne (71). These products were obtained from the dibromide of 5,6,7,8-tetrachlorotetralin, and from 1,1,2,3,4,4-hexachlorotetralin respectively by reaction with alcoholic sodium ethoxide.

Armstrong and Wynne (4) have also reported the preparation of 1,3,8-trichloronaphthalene by direct chlorination of 1-nitronaphthalene.

Buffle and Corbaz (19) employed a slightly different technique involving the chlorination of 1-nitronaphthalene in various solvents, in the presence of iodine or ferric chloride, followed by evaporation of the solvent. Fractional crystallization, steam distillation, and distillation at ordinary pressures proved unsuccessful, so vacuum distillation was used to separate the reaction mixture into pure products.

Heating to 100-105° resulted in decomposition with the evolution of hydrochloric acid fumes and nitrogen dioxide. Following this, the temperature was raised, and the various fractions were collected. From these fractions naphthalene, 1-chloronaphthalene, 1,3,5-trichloronaphthalene, and unidentified dichloronaphthalene, and a compound described as a tetrachloro-nitronaphthalene melting at 176.5°, were isolated.

Weissberger, Sangelwald, and Hampson (79) have used the method of Atterberg (7) to prepare 1,5-dichloronaphthalene.

b. Reactions of 8-chloro-1-nitronaphthalene.

According to Vorozhtsov and Koslov (77), 8-chloro-1-nitronaphthalene undergoes partial hydrolysis to 8-chloro-1-naphthol on boiling with water, or during steam distillation.

Ullmann and Consonno (72) reduced 8-chloro-1-nitronaphthalene to 8-chloro-1-naphthylamine, using tin and hydrochloric acid. This method was very tedious, and gave poor yields. Adams and Steele (1) developed a convenient method of reduction using iron powder and water, with a little hydrochloric acid, to give yields of up to 97% of the amine.

Weissberger, Sangelwald, and Hampson (79) have reported the diazotization of 8-chloro-1-naphthylamine to give 1,8-dichloronaphthalene, according to the method of Atterberg (9), while Willstaedt and Scheiber (80) reported the preparation of 8-chloro-1-iodonaphthalene by reaction of the diazotized amine with potassium iodide. Bergmann and Hirschberg (15) prepared 8-chloro-1-fluoro-, 1,8-dichloro-, 1-bromo-8-chloro-,

8-chloro-1-iodo-, and 8-chloro-1-cyanonaphthalene by treatment of the diazotized amine with borofluoric acid, cuprous chloride, cuprous bromide, potassium iodide, and potassium cuprocyanide respectively.

Feiser and Seligman (32) prepared 1-bromo-8-chloronaphthalene in a better yield than Bergmann and Hirschberg, by modifying the procedure used. The Grignard reagent prepared by reacting 1-bromo-8-chloronaphthalene with one mole of magnesium, on methylation with methyl sulphate, gave 8-chloro-1-methylnaphthalene. Feiser and Bowen (31) repeated this work, obtaining improved yields of the bromo-chloro- and chloro-methylnaphthalenes by using specially purified reagents.

c. Bromination of 1-nitronaphthalene.

In contrast to chlorination, the bromination of 1-nitronaphthalene seems to follow a well directed course, leading to bromo-nitronaphthalenes as the only products.

Guareschi (40) was probably the first worker to report the bromination of 1-nitronaphthalene. He obtained two bromo-nitronaphthalenes, the 5-bromo isomer melting at 122.5° , and what was likely the 8-bromo isomer, melting at about 100° . Meldola and Streatfield (56) have prepared 8-bromo-1-nitronaphthalene from 1-nitro-8-naphthylamine by the Sandmeyer reaction, and report its melting point as $99-100^{\circ}$. Both the above products were quite stable in the presence of excess bromine at 100° .

Scheufelin (64), Ullmann and Consonno (72), Shoesmith and Rubli (67), Hill, Short and Stromberg (42), McLeish and Campbell (55), and Price and Voong (63) have prepared 5-bromo-1-nitronaphthalene by the bromination of molten 1-nitronaphthalene. Attempts by McLeish and Campbell to isolate the 8-bromo derivative by this method were unsuccessful, while Price and Voong have obtained yields of 80-85% of the 5-bromo-1-nitronaphthalene.

(4) Reactions of Sulphonic Acids.

A fourth method of obtaining substituents in the 1,8-positions in naphthalene consists in the nitration of 1-naphthalenesulphonic acid or 1-naphthalenesulphonyl chloride.

Vorozhtsov and Gribov (76) have reported that the principal products in the nitration of 1-naphthalenesulphonic acid are 5- and 8-nitro-1-naphthalenesulphonic acid, while Steiger (69) has reported that 8-nitro-1-naphthalenesulphonyl chloride is the principal product in the nitration of 1-naphthalene sulphonyl chloride.

A number of patents (62) have been described for the nitration of 1-naphthalenesulphonic acid, and reduction to the mixture of amino-sulphonic acids. The 8-naphthylamine-1-sulphonic acid may be separated by treating the neutral or alkaline solution of the salts with alkali metal bisulphites, which give the right pH for precipitation of this

isomer without the precipitation of the other isomers present. 8-Naphthylamine-1-sulphonic acid is commercially available under the name of "peri-acid".

8-Nitro-1-naphthalenesulphonic acid and 8-naphthylamine-1-sulphonic acid may undergo various reactions leading to the preparation of 1,8-dihalonaphthalenes.

a. Reactions of 8-nitro-1-naphthalenesulphonic acid.

Cleve (24) reported that when the potassium salt of 8-nitro-1-naphthalenesulphonic acid was mixed with phosphorus pentachloride in a solution in carbon disulphide, nitrous fumes were produced, and 8-chloro-1-naphthalenesulphonyl chloride was obtained. Armstrong and Wynne (4) found that on heating this latter compound at 200-230° as long as sulphur dioxide was evolved, a large amount of 1,8-dichloronaphthalene was obtained.

I.G. Farbenind (29) described a patent for the preparation of 1-bromo-8-chloronaphthalene from 8-chloro-1-naphthalenesulphonic acid by treatment with halogens or compounds yielding halogens, which replace the sulphonic acid group.

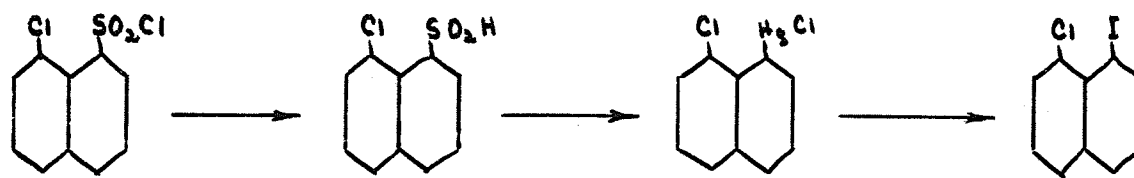
Kalle (51) has described a patent for the preparation of 1-chloro-8-nitronaphthalene from 8-nitro-1-naphthalenesulphonic acid by the action of chlorine, hydrochloric acid, sodium, and chlorate or a hypochlorite. Freidlander, Karamessinin, and Schenk (37) have also prepared this compound by the treatment of hot hydrochloric acid solutions of 8-nitro-1-naphthalenesulphonic acid with sodium chlorate. Vorozhtsov and Koslov (77), using this method, have reported the isolation

of two crystalline forms of 1-chloro-8-nitronaphthalene melting at 93-94° and at 125°. The reactions involved in the preparation of dihalonaphthalenes from 1-chloro-8-nitronaphthalene have been described in the section on the chlorination of 1-nitronaphthalene.

b. Reactions of 8-naphthylamine-1-sulphonic acid.

Cumming and Muir (25) have prepared 8-chloro-, 8-bromo-, and 8-iodo-1-naphthalenesulphonic acids and the corresponding sulphonyl chlorides by diazotization of 8-naphthylamine-1-sulphonic acid, and coupling with suitable reagents. Beattie and Whitmore (12) have prepared 8-chloro-1-naphthalenesulphonyl chloride in kilogram quantities, and have developed a unique method of preparation of the dihalo-naphthalenes from this compound. The sulphonyl chloride was reduced to the sulphinic acid with sodium sulphite and sodium hydroxide. 8-Chloro-1-naphthylmercuric chloride was prepared by boiling the sulphinic acid with aqueous mercuric chloride. The mercuri-bis-chloronaphthalene was prepared from the mercuri-chloride by treatment with an excess of alcoholic sodium iodide. The 8-chloro-1-naphthylmercuric bromide and iodide were obtained in a similar way. All these mercuri-compounds were prepared in yields of over 80%.

In another paper (13), these authors have described the preparation of 8-chloro-1-iodonaphthalene in good yield by treating 8-chloro-1-chloromercuri-naphthalene with iodine and sodium iodide in alcohol.



From the foregoing survey, it is evident that a considerable variety of reactions might lead to the desired products for use in this investigation. The chlorination of 1-nitronaphthalene, and the subsequent reactions leading to the preparation of 1,8-dichloronaphthalene and 1-bromo-8-chloronaphthalene seemed to be the most direct, and these methods have been used in the present attempt to prepare 1,8-dimethylnaphthalene.

EXPERIMENTAL WORK.

A Preparation of 8-chloro-1-nitronaphthalene.

The chlorination of molten 1-nitronaphthalene according to the method in the literature (72), for the preparation of 8-chloro-1-nitronaphthalene, has been found to present considerable difficulty. The variations tried are indicated elsewhere in this report. For the preparation of 8-chloro-1-nitronaphthalene, the following procedure was employed:

Technical 1-nitronaphthalene (200 gm.) was intimately mixed with powdered ferric chloride (4 gm.) in a one litre flask, and melted at 60° on the water bath. Chlorine from a cylinder was passed into the molten mass until the gain in weight was 44 gm. The resulting dark colored oil was washed repeatedly with warm water (60°) until the washings had very little color, the water was decanted off, and the resulting light colored oil was allowed to stand overnight, or for several days. Very small crystals separated out from the oil, and were collected by filtering with suction on a fine sintered glass Buchner funnel.

The pasty mass was crystallized from a mixture (300 cc.) of equal volumes of benzene and ligroin (B.P. $60-80^{\circ}$), decolorizing with Norite; or better, dissolved in hot benzene (150 cc.), decolorized with Norite, cooled to room temperature, and the 8-chloro-1-nitronaphthalene precipitated with ligroin (150 cc.). The resulting product, melting at $84-88^{\circ}$ *, was used in the work which follows. The yield was 47-62 gm., 20-26%.

* All melting points are uncorrected.

A sample recrystallized from benzene-ligroin melted at 91.5-93°. (Literature melting point 94°). For X-ray powder photograph of 8-chloro-1-nitronaphthalene see Page 65.

B Preparation of 8-chloro-1-naphthylamine.

8-Chloro-1-nitronaphthalene was reduced according to the method of Adams and Steele (1).

8-Chloro-1-nitronaphthalene (20 gm.) was intimately ground with powdered iron (60 gm.), and placed in a 500 cc. round bottomed flask fitted with a reflux condenser. Water (30 cc.) was added, and the mixture was heated to boiling for 10 minutes on the waterbath. A few drops of concentrated hydrochloric acid were added, the mixture was thoroughly shaken, and heating on the waterbath was continued for seven hours, with occasional shaking.

When reduction was complete, the solid mixture was extracted with boiling alcohol in three 100 cc. portions and one 50 cc. portion, until the filtrate gave no cloudiness with water. The alcoholic solutions were poured into a large amount of water (2-3 litres) and the crude amine was collected on a filter. The crude amine was purified by dissolving it in warm dilute hydrochloric acid (25 cc. concentrated hydrochloric acid in 2 litres of water), filtering to remove unreduced chloronitronaphthalene, decolorizing with Norite, cooling with ice, and reprecipitating the 8-chloro-1-naphthylamine with concentrated ammonia. The tan colored product melted at 87.5-

89°, yield 10-12 gm. (58-70%). Crystallization from ligroin (25 cc./gm.) gave long white needles, turning pink on exposure to the air, melting at 91.5-93°. (Literature melting point 95-96°). For X-ray powder photograph of this amine see Page 66 .

C Preparation of 1-bromo-8-chloronaphthalene.

Method of Feiser and Seligman (32).

8-Chloro-1-naphthylamine (16.5 gm.) was dissolved in hydrobromic acid (25 cc., S.G.1.49) and water (125 cc.) The solution was cooled below 5°, and a solution of sodium nitrite (7.0 gm.) in water (25 cc.) was added slowly. The solution was allowed to stand for half an hour with occasional stirring.

The diazotized solution was added to a cooled solution of cuprous bromide (30.gm.), sodium bromide (4 gm.) and copper wire (3.5 gm.) in hydrobromic acid (25 cc., S.G. 1.49) and water (5 cc.). The mixture was stirred well, and allowed to stand overnight. The mixture was then heated to 75° on the waterbath, and a frothy material separated. This was extracted with ether (400 cc.) and an attempt was made to purify it by washing the ethereal solution with dilute hydrochloric acid. The aqueous extracts remained purple colored, even after use of 1500 cc. of acid. After washing the ethereal solution with 10% sodium hydroxide solution in three 100 cc. portions, it was dried with calcium chloride, and the ether was evaporated.

Large brown crystals were obtained which, on recrystallization from alcohol (10 cc./gm.) gave small yellow crystals

melting at 94-96.5°, yield 3.7 gm. (16.5%). (Literature melting point 96.5-97°).

Several modifications of this procedure were tried. It was found that dissolving the crude product in benzene, and washing the benzene solution with acid and alkali, resulted in emulsification and loss of the product. Steam distillation from an alkaline solution proved to be very tedious. The following procedure was found to be the most satisfactory.

8-Chloro-1-naphthylamine (30 gm.) was dissolved in hydrobromic acid (45 cc., S.G. 1.49) and water (200cc.) and diazotized with sodium nitrite (13 gm.).

A cuprous bromide solution was prepared from crystallized copper sulphate (125 gm.), sodium bromide (73 gm.) and water (420 cc.) by the reduction of a boiling solution of the above with sodium sulphite (39 gm.) added slowly. The solution was then cooled slowly, and the liquid was decanted. The white solid was washed twice by decantation with water containing a little sulphurous acid, and the cuprous bromide was partially dissolved in hydrobromic acid (75 cc., S.G. 1.49) and water (55 cc.).

The cuprous bromide solution, in a two litre flask set for steam distillation, was heated to boiling, and the diazotized solution of the amine was added slowly through a small funnel leading to the bottom of the flask, while steam was passed through the solution. Steam distillation was continued

until no more solid distilled over, and the product was made alkaline with solid sodium hydroxide. The crude solid product (21.9 gm.) was collected by filtering with suction, crushed in a mortar with more 10% sodium hydroxide solution, washed with water, and dried.

The crude 1-bromo-8-chloronaphthalene was distilled under reduced pressure (B.P. 210-220°/50 mm.) and then recrystallized from alcohol, to give white crystals melting at 95.5-97°, yield 13 gm. (32%) Further product (1.5 gm.) melting above 93° was recovered from the mother liquors. For X-ray powder photograph of 1-bromo-8-chloronaphthalene see Page 66.

D Preparation of 1,8-dichloronaphthalene.

Modification of the method of Bergmann and Hirschberg (15).

8-Chloro-1-naphthylamine (30 gm.) was diazotized in water (200 cc.) and concentrated hydrochloric acid (41.5 cc.) with sodium nitrite (13 gm.) at 0-5°.

Cuprous chloride was prepared as follows:

Crystallized copper sulphate (125 gm.) was dissolved in boiling water (400 cc.) and sodium chloride (38 gm.) was dissolved in the hot solution. A solution of sodium bisulphite (27 gm.), sodium hydroxide (18 gm.), and water (200 cc.) was added to the hot solution, and sodium sulphite (26 gm.) was added to complete the reduction, giving a colorless solution. The solution was cooled, the liquid was decanted, and the

solid cuprous chloride was washed twice by decantation with 300 cc. portions of water containing a little sulphurous acid.

The wet cuprous chloride was dissolved in concentrated hydrochloric acid (175 cc.) and the solution was heated to boiling. The diazotized solution of 8-chloro-1-naphthylamine was added slowly to the boiling solution, through a funnel leading to the bottom of the flask. The nitrogen was expelled rapidly, and a black oil separated. This was steam distilled until four litres of distillate were collected. The solid crude 1,8-dichloronaphthalene was filtered off and air dried.

This crude product was finely pulverized, and washed with 10% sodium hydroxide solution. The dried 1,8-dichloronaphthalene was recrystallized from alcohol (180 cc.) giving light gray crystals melting at $83.5-86^{\circ}$, yield 18.9 gm. (57%). A sample twice recrystallized from alcohol gave white crystals melting at $88.5-89^{\circ}$. (Highest literature melting point $89-89.5^{\circ}$). For X-ray powder photograph see Page 66.

E Attempted preparations of 1,8-dimethylnaphthalene.

Several attempts were made to prepare 1,8-dimethylnaphthalene through Grignard reactions on 1,8-dichloronaphthalene and 1-bromo-8-chloronaphthalene.

(1) 1,8-Dichloronaphthalene (1.97 gm., 0.01 mole) in anhydrous ether was added to magnesium turnings (0.515 gm., 0.021 mole). The Grignard reaction was started by the addition of

a few drops of the Grignard reagent from methyl iodide and magnesium. The reaction proceeded very slowly, forming a white precipitate of the insoluble Grignard reagent. Even after refluxing for eight hours, considerable magnesium was still unreacted.

A solution of methyl iodide (1.3 cc., 0.02 mole) in anhydrous ether was added. This caused the rest of the magnesium to go into solution. Refluxing was continued for six hours. The solution was poured into dilute sulphuric acid, more ether was added, and the ethereal solution was separated and dried with magnesium sulphate. The residue on evaporation was a grayish yellow solid (1.57 gm.) melting at $78-80^{\circ}$. The mixed melting point with pure 1,8-dichloronaphthalene was $80-82^{\circ}$.

(2) The Grignard reagent was prepared from methyl iodide (1.9 cc.) and magnesium turnings (0.735 gm.) in anhydrous ether (25 cc.). This solution was refluxed for 15 minutes after the reaction had ceased, most of the magnesium having gone into solution. A solution of 1,8-dichloronaphthalene (1.97 gm.) in anhydrous ether (15 cc.) was added, the mixture was refluxed for 45 minutes, and then allowed to stand overnight. The Grignard complex was decomposed with dilute hydrochloric acid, and the ethereal layer was dried and allowed to evaporate. The residue was a yellow solid (1.83 gm.) melting

at 78-80°.

This was recrystallized from alcohol (15 cc.), the alcoholic solution, after decolorization, being cooled in ice. The white crystals obtained by filtration (1.20 gm.) melted at 83.5-85°. The mixed melting point with 1,8-dichloronaphthalene was 85-86°.

The filtrate was evaporated to a volume of about 0.5 cc., and again cooled in ice, to give yellowish gray crystals (0.22 gm.) melting at 75-78°. On evaporation to dryness, a further amount (0.02 gm.) of this material was obtained. Due to the meagre yield of this lower melting fraction, no attempt was made to purify it further.

(3) An attempt was made to prepare the Grignard reagent from 1-bromo-8-chloronaphthalene (2.41 gm., 0.01 mole) and magnesium turnings (0.515 gm., 0.021 mole) in anhydrous ether (50 cc.). The reaction proceeded very slowly, as the Grignard reagent formed white crystals which were almost insoluble in ether. When the reaction had ceased (much unreacted magnesium), a solution of methyl iodide (1.9 cc., 0.03 mole) in anhydrous ether (15 cc.) was added. The rest of the magnesium dissolved, and a yellow material precipitated from the solution.

After refluxing for 45 minutes, the ether solution was poured into dilute sulphuric acid and ice. More ether was added, and the aqueous solution was saturated with salt before separation of the ethereal layer. This was dried with calcium chloride and evaporated. The residue, on solution

in alcohol (10 cc.) gave a yellow solution which showed green fluorescence. On dilution with water, yellow crystals (0.46 gm.) were obtained melting at 50-57°. The crystals gave a white fluorescence in ultra-violet light, while the filtrate gave a bluish-white fluorescence. A second recrystallization from dilute alcohol gave white crystals (0.30 gm.) melting indefinitely at about 80°. A sodium fusion gave a positive test for bromine.

1-Bromo-8-chloronaphthalene does not give any fluorescence with ultra-violet light, so that a fluorescent compound, possibly perylene, is present along with impure 1-bromo-8-chloronaphthalene in the above product. This was not investigated further.

(4) The Grignard reagent was prepared from 1-bromo-8-chloronaphthalene as above, with the addition of dry benzene (50 cc.) to help keep the sparingly soluble Grignard reagent in solution. After refluxing for 2½ hours, there was still unreacted magnesium, but the solution had a yellow-brown color.

Practical methyl sulphate (4.5 cc., 0.048 mole) in dry benzene (15 cc.) was added to the Grignard solution, which was then refluxed for one hour. The solution was poured into dilute sulphuric acid; the organic layer was washed with sodium carbonate solution, then with water, and dried with magnesium sulphate.

On evaporation, a black oil (0.5 cc.) was obtained, which would not solidify at -20°. This oil was distilled under reduced pressure, giving a creamy yellow liquid. An

Attempt to prepare the picrate derivative from this product was unsuccessful.

(5) 1-Bromo-8-chloronaphthalene (7.245 gm.) was dissolved in anhydrous ether (250 cc.) and added slowly to magnesium turnings (1.485 gm.) contained in a 500 cc. three-necked round bottom flask, fitted with a mercury sealed stirrer, a reflux condenser, and a dropping funnel. After addition of the etheral solution, refluxing and stirring were continued for 6 hours, following which the mixture stood at room temperature for 14 hours. Dry benzene was added during the reaction, to help keep the crystalline Grignard reagent in solution. Some unreacted magnesium remained in the mixture.

A solution of practical grade methyl sulphate (13 cc.) in dry benzene was added slowly to the Grignard solution, producing some heat. The mixture was stirred and refluxed, after which most of the ether was distilled off. The resulting benzene solution was allowed to stand for 20 hours, becoming very thick.

The Grignard complex was decomposed with dilute hydrochloric acid, and the benzene layer was washed with 10% sodium hydroxide solution in two 125 cc. portions, to remove the excess methyl sulphate. The benzene solution was dried, and the solvent was distilled off at normal pressure. The residue was then vacuum distilled, and separated into two fractions: The first, boiling below $82^{\circ}/19$ mm., weighed 2.3 gm. The second, boiling at $82-130^{\circ}/19$ mm., weighed 3.5 gm. These two fractions, both orange-red in color, remained

liquid at -20° .

The boiling points of these two fractions seem quite low, considering that the reported boiling point for 1,8-dimethylnaphthalene is $140^{\circ}/18$ mm., while that for 8-chloro-1-methylnaphthalene is $125^{\circ}/4$ mm. It may be that 1-methylnaphthalene, or the benzene solvent, may form an azeotropic mixture with the desired product, causing this lowering of the boiling point below that for either of the expected products. The boiling point of the starting material would be much higher, since it is reported as $154^{\circ}/4$ mm.

Lack of time prevented further investigation of this question.

F The chlorination of 1-nitronaphthalene.

Since considerable difficulty has been encountered in the present investigations of the preparation of 8-chloro-1-nitronaphthalene by the chlorination of 1-nitronaphthalene, a special study of this reaction was undertaken, in an attempt to find the most convenient procedure for the preparation of this product.

(1) Pure 1-nitronaphthalene (20 gm.) was mixed with powdered ferric chloride (0.4 gm.) and melted on the water bath at $55-65^{\circ}$. Chlorine was passed into the molten mass until the gain in weight was 4.4 gm. The oily reaction product was washed with water, and an attempt was made to crystallize the pasty mass from alcohol. Most of the product separated from the alcoholic solution as a red oil, while very pale yellow crys-

tals formed on the surface of this oil after further cooling. These were filtered off and melted at 84-87° after two recrystallizations from alcohol. Yield 0.5 gm.

An attempt was made to steam distill the oily residue after evaporation of the alcohol. No material distilled over, but the residue turned blackish yellow, showing considerable decomposition.

(2) 1-Nitronaphthalene (50 gm.) was mixed with ferric chloride (11.0 gm.), melted on the water bath at 50-60°, and chlorine was passed into the molten mass until the gain in weight was 11.0 gm.

In one run, the reaction mixture was subjected to vacuum distillation. On heating, the oily material turned black, and frothed badly, with a great deal of decomposition taking place below 130°.

In other runs, the reaction product was dissolved by warming in alcohol (200 cc.) and then left in the refrigerator overnight. The red oil which first separated froze solid. Yellow crystals the separated from the alcoholic solution, and were collected by scraping them from the frozen oil, and filtering with suction. By repeating this dissolving and freezing out, 8 gm. of yellow needle-like crystals were obtained, melting at 27-32°. Two recrystallizations from alcohol gave crystals melting at 32-34°, with no change in melting point on further recrystallizations. Prolonged vacuum dessication raised the melting point to 35-37°.

A sodium fusion indicated that nitrogen and chlorine

were present in this product. An analysis for chlorine by the method of Bobranski and Sucharda (16) gave Cl:9.02, 7.78%. Calculated for $C_{10}H_6NO_2Cl$: Cl:17.08%.

Though these analyses do not give good agreement, they seem to indicate that the chlorine content is about half that for chloronitronaphthalene, suggesting that the product might be a double compound or dimer, containing only one chlorine atom. The low melting point, however, seemed to make this questionable. A molecular weight determination by the Rast method gave a value of 195, while that for chloronitronaphthalene is 207.5, and that for nitronaphthalene is 173, which confirmed that this product is only a monomer in size.

The only remaining explanation for the low chlorine content seemed to be that, in spite of the constant melting point after repeated crystallizations from alcohol, the product was a mixture. Recrystallization of the product from ligroin, or from benzene-ligroin mixtures, gave fine pale yellow needles, which had an indefinite melting point over the range 46-70°, confirming that the product was actually a mixture.

The residual oil after filtering off the above product deposited a small amount of yellow solid after standing for several weeks at room temperature. This, on two recrystallizations from alcohol, melted at 88-90°, yield less than 0.5 gm. A sodium fusion indicated the presence of nitrogen and chlorine. A chlorine analysis gave Cl:15.88%, calculated for $C_{10}H_6NO_2Cl$: Cl:17.08%. This product is therefore impure 8-chloro-1-nitronaphthalene.

In two other trials, the whole mass from the chlorination of 1-nitronaphthalene was stirred vigorously in cold water until it became quite pasty. Attempted recrystallization of this pasty mass from alcohol, or from a mixture of equal volumes of benzene and ligroin, gave crystals melting indefinitely in the range 45-85°.

It was finally discovered that the use of a technical grade of 1-nitronaphthalene gave a chlorinated product which crystallized readily, as suggested in the literature, and from which the desired 8-chloro-1-nitronaphthalene could be separated conveniently, as described in the preparation of this compound on Page 25.

(3) Chlorination in CCl₄ at Room Temperature.

1-Nitronaphthalene (10 gm.) was dissolved in carbon tetrachloride (75 cc.) at room temperature, and ferric chloride (0.2 gm.) was added. Chlorine was bubbled through the solution for 1-1½ hours, using a gas dispersion tube. The solution was filtered, and the solvent was distilled off, or evaporated at the suction pump. The product obtained was pale yellow crystals (9.3 gm.) of slightly impure 1-nitronaphthalene melting at 49-53°. Similar experiments using a clean iron nail or anhydrous aluminum chloride (0.5 gm.) as halogen carrier resulted in the recovery of 9.3 and 9.9 gm. respectively, of 1-nitronaphthalene, melting at 52-55°.

(4) Chlorination in boiling Carbon Tetrachloride.

The quantities used were as above, with ferric chloride (0.3 gm.) as halogen carrier, the solution being kept at a gentle boil during the chlorination. After distillation of the solvent, the dark colored oily residue was well washed with water, and taken up in ether, which was evaporated to give a rather greasy solid melting at 31-40°. Recrystallization from alcohol gave only material melting below 50°.

(5) Distillation of the residual oil from the chlorination of 1-nitronaphthalene.

The residual oil from the chlorination of 1-nitronaphthalene after filtering off the 8-chloro-1-nitronaphthalene, as described on Page 25, was washed with warm water, which was then decanted off, and the oil was dried by the addition of calcium chloride. The drying agent was filtered off, and 302 gm. of the oil was placed in a 500 cc. Claisen Flask with an asbestos-insulated side arm, and vacuum distilled.

Fraction A came over at 176-190°/18-20 mm. There was little evidence of decomposition taking place, the distillate being a yellow oil which partly solidified in the receiver. This product was filtered to remove the solid (I) present, (melting below 40°) 26 gm., from the residual oil (II) 132 gm.

Fraction B had a boiling point of 194-206°/17-18 mm. This fraction showed considerable indication of decomposition, becoming redder in color as the distillation was continued. This fraction went partially solid on standing, but the solid was too fine grained to filter. The material developed a strong odor of hydrochloric acid on standing in a closed bottle.

Fraction A(I) was recrystallized from alcohol (150 cc.) giving much oily material and the following solid fractions:

- (1) Coarse powdery crystals M.P. 40-44°. Yield 7.6 gm.
- (2) Yellow silky needles M.P. 44-50°. Yield 4.2 gm.
- (3) Yellow needles M.P. 39-46°. Yield 2.5 gm.
- (4) Yellow needles M.P. 36-46°. Yield 1.3 gm.

A sodium fusion of fraction (2) gave a negative test for halogen. The X-ray powder diffraction pattern of this fraction was similar to that from an authentic sample of 1-nitronaphthalene. The boiling point of the whole fraction A was also in agreement with the boiling point of 168.5°/12 mm. as given by Buffle and Corbaz (19). All these fractions are therefore presumably impure 1-nitronaphthalene.

Fraction A(II) deposited more of the above solid on standing for some time at room temperature. This was filtered off, and the oil (112 gm.) was redistilled, giving the following fractions:

- (1) B.P. 176-180°/16 mm. Yield 45.0 gm.
- (2) B.P. 180-185°/16 mm. Yield 21.7 gm.
- (3) B.P. 186-200°/16 mm. Yield 22.7 gm.

Fraction (1) was a greasy solid at room temperature. A portion of this was washed with ligroin, and pressed dry on filter paper. It melted at 40-45°, while the mixed melting point with 1-nitronaphthalene was 42-48°. The identification of these fractions as 1-nitronaphthalene indicated that much of the original material escaped chlorination.

Fraction (2) distilled chiefly at 183-184°, giving a yellow oil which largely solidified on standing at room temperature for three weeks.

Fraction (3) was darker in color, and solidified on standing. These fractions, and Fraction B, have not been further investigated, due to lack of time.

G. Bromination of 1-nitronaphthalene.

The bromination of 1-nitronaphthalene (fused) with bromine has been reported to give 5-bromo-1-nitronaphthalene and 8-bromo-1-nitronaphthalene, the former being the most abundant. It was hoped that bromination in a solvent might increase the yield of the 8- isomer, but only 5-bromo-1-nitronaphthalene was isolated. The bromination was carried out as follows:

1-Nitronaphthalene (10 gm.) was dissolved in warm carbon tetrachloride (40 cc.) in a flask fitted with a reflux condenser and a small dropping funnel. Ferric chloride (0.3 gm.) was added, and the solution was brought to a gentle boil on the steam bath. Bromine (3.3 cc.) was added through the dropping funnel over a period of one hour, the mixture was refluxed for one hour further, and the solvent was distilled off. The molten material obtained was poured into water containing sodium bisulphite, and crushed to remove the excess bromine. The crude product (14.6 gm.) was filtered with suction. Two recrystallizations from alcohol gave very pale yellow crystals (6.4 gm.) melting at 121-122°, while a small additional yield was obtained by evaporating the mother liquor. The literature melting point of 5-bromo-1-nitronaphthalene is 122.5°. For X-ray powder photograph see Page 65.



H Nitration of 1-nitronaphthalene.

(1) Method of Hodgson and Walker (46).

1-Nitronaphthalene (25 gm.) was dissolved in concentrated sulphuric acid (100 cc.) in a 500 cc. round bottom flask, and nitrated below 10°C by the gradual addition of a mixture of one volume of concentrated nitric acid and five volumes of concentrated sulphuric acid, until the mixture turned to a straw color. The mixture was shaken or stirred repeatedly during the addition of the nitrating acid, of which about 70 cc. was required. The nitrating mixture was poured on ice, and the precipitated dinitronaphthalene was washed free from acid, being left in paste form for interaction with a reducing agent.

The nitrated mixture was stirred with water (200 cc.), and treated over 15 minutes at about 90° , with a solution of sodium sulphide (11.6 gm.) and flowers of sulphur (3.1 gm.) in water (40 cc.), followed by stirring at 90° for 20 minutes more. After cooling, the solid was collected on a sintered glass filter funnel, and washed with water. The 5-nitro-1-naphthylamine was removed by three extractions with boiling solutions of concentrated hydrochloric acid (25 cc.) in water (350 cc.).

The residue was boiled with two portions of benzene (250 cc. and 50 cc.). The brown crystals (17 gm.) obtained on cooling and evaporating the benzene solutions melted at $125-135^{\circ}$. Recrystallization from alcohol (600 cc.) raised the melting point to $140-150^{\circ}$, while recrystallization from benzene gave bright yellow crystals melting at $150-155^{\circ}$, with

no change in melting point on further recrystallizations from this solvent.

(2) Modification of Hodgson and Whitehurst (48).

The nitration was carried out as above, using double quantities, but the nitrated mixture was heated slowly to 90-100°, when solution was complete. The solution was run in a thin stream into an ice water mixture, and stirred for one hour. The fine paste was removed and washed with water, then with dilute ammonia until the washings were alkaline, and finally with more water. The paste was dried in the oven, and the powdered material was used in the following experiments.

(a) Separation of isomers: Method of Hodgson and Ward (47).

The finely powdered mixture of dinitronaphthalenes (10 gm.) was suspended in boiling methyl alcohol (150 cc.) and treated with 14 cc. of a reagent prepared by solution of sodium sulphide (24 gm.) and sodium bicarbonate (8 gm.) in water (40 cc.). The reducing agent was added in one batch, and boiling was continued for 5 minutes. Ice chips were added to the red-brown mixture before pouring it into water (750 cc.).

The solid was filtered off, washed with water, extracted with four 400 cc. portions of boiling 8% hydrochloric acid, rewashed with water, and dried. The dried residue was extracted with two 200 cc. portions of boiling toluene, the combined toluene extracts were boiled with bone charcoal, and filtered. On cooling, orange-brown prisms (2.8 gm.) melting at 159-165° were obtained. One recrystallization from benzene gave tan colored crystals (0.5 gm.) melting at 168-171°.

The literature melting point for pure 1,8-dinitronaphthalene is 170.5° . The rest of the solid recovered by boiling down the toluene solution was dark colored, and of much lower melting point.

(b) Method of Callotti and Galimberti (38).

The powdered mixture of dinitronaphthalenes (20 gm.) in concentrated sulphuric acid (357 gm.) and 20% oleum (143 gm.) (ie 500 gm. of 100% H_2SO_4) was heated at 45° for one half hour during the addition of flowers of sulphur (5 gm.). The temperature was then raised to $85-90^{\circ}$, and held for two hours. The mixture was cooled, poured onto ice, filtered, and the residue crystallized from glacial acetic acid, giving gray-pink crystals (13.7 gm.) melting at $135-146^{\circ}$. Recrystallization of 11.1 gm. of this product from toluene (225 cc.) gave dirty gray crystals (6.3 gm.) melting at $155-161^{\circ}$. A second recrystallization from toluene gave no increase in melting point.

In the above nitrations of 1-nitronaphthalene, very little pure 1,8-dinitronaphthalene was isolated. Hodgson and Whitehurst (48) give a setting point of 152° for a mixture of 90% of 1,8-dinitronaphthalene with 10% of the 1,5-isomer, so that the products obtained above must contain at least 90% of the desired isomer.

Since the preparation of 8-chloro-1-nitronaphthalene seemed to indicate a convenient method of preparation of 1,8-dihalonaphthalenes, no further work on nitration was done.

DISCUSSION OF RESULTS.

A Mechanisms for the Chlorination of 1-Nitronaphthalene.

Due to the fact that chlorination of 1-nitronaphthalene gives rise to naphthalene and polychloronaphthalenes, as well as the expected chloronitronaphthalenes, several mechanisms have been proposed to explain the formation of these other products. Atterberg (7) described the oil obtained in the chlorination of 1-nitronaphthalene as an addition compound, which evolved hydrogen chloride and reddish vapors on heating. He suggested that the nitro group was removed first, and that this, on reaction with the liberated hydrogen chloride, gave nascent chlorine, which influenced substitution.

Buffle and Corbaz (19) have observed similar phenomena on heating the chlorinated product to 100-105°, resulting in the evolution of hydrogen chloride, which became progressively more reddish in color as decomposition proceeded. These authors have suggested a slightly different mechanism. They propose that chlorine is absorbed by the 1-nitronaphthalene, forming addition and substitution products simultaneously. The addition products (chlorides of 1-nitronaphthalene) are unstable to heat, decomposing with the liberation of hydrogen chloride and possibly chlorine. This chlorine possesses great reactivity, and drives the nitro group out of the molecule. This nitro group, in the form of nitrogen dioxide, forms the red fumes observed. Buffle and Corbaz have established that 1-nitronaphthalene, 5-chloro-1-nitronaphthalene, and 8-chloro-1-nitronaphthalene are stable to heat, undergoing no decomposition at temperatures exceeding 360°.

Before developing a more detailed explanation for the various products obtained in the chlorination of 1-nitronaphthalene, a summary of these products and their properties will be presented.

TABLE II

<u>Product</u>	<u>M.P.</u>	<u>Reference.</u>
5-chloro-1-nitronaphthalene	111°	(33)(77)
8-chloro-1-nitronaphthalene	94°	(72)(77)
5,8-dichloro-1-nitronaphthalene	93°	(11)
tetrachloronitronaphthalene	176.5°	(19)
naphthalene	80°	(19)
1-chloronaphthalene	liquid	(7)(77)
1,5-dichloronaphthalene	167°	(7)
1,3,5-trichloronaphthalene	103°	(7)
1,4,5-trichloronaphthalene	131°	(78)
1,3,8-trichloronaphthalene	90°	(7)
tetrachloronaphthalene	194°	(7)

It will be immediately noticed that in all the above products in which the positions of the substituents have been established, one of the rings in the naphthalene nucleus has no more than one substituted group, this being in the alpha position. It will also be noted that in several of the compounds, chlorine is found in one of the beta positions. Any mechanism for the chlorination of 1-nitronaphthalene must indicate clearly the methods by which each of these compounds are formed.

In order to develop such a mechanism, a study of the

chlorination of naphthalene itself will prove useful. The chlorination of naphthalene has been a subject of study for many authors, but the works of some of these authors seem to have a more direct bearing of the present investigation.

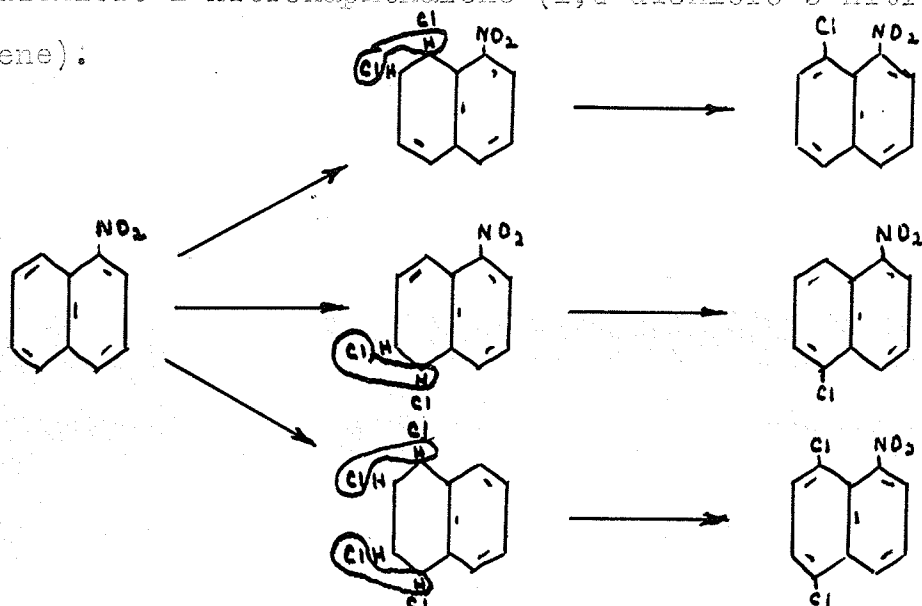
Faust and Saame (30) prepared 1,2,3,4-tetrachlorotetralin by chlorination of naphthalene. By boiling this product with alcoholic potassium hydroxide, the 1,3-, 1,4-, and 2,3-dichloronaphthalenes were obtained. Krafft and Becker (52) obtained the 1,2- and 1,4-dichloronaphthalenes by simply heating the tetrachloride.

More recently, Ferrero and Wunenburger (34) have reported that chlorination of naphthalene gives a dichloride and a tetrachloride, with all the chlorine atoms on the same ring. These compounds lose hydrogen chloride on heating to yield 1-chloronaphthalene and 1,4-dichloronaphthalene respectively. These authors suggest that halogen can be introduced into the beta positions of the naphthalene nucleus only by indirect methods, such as the Sandmeyer reaction.

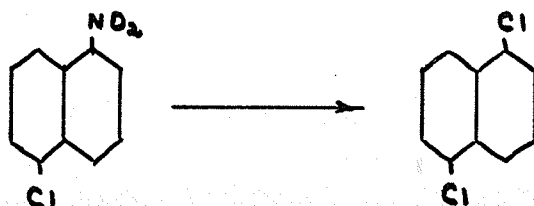
This concept of naphthalene first forming addition compounds on chlorination, with the subsequent loss of hydrogen chloride, can be conveniently applied to the chlorination of 1-nitronaphthalene. The probable mechanism is this:

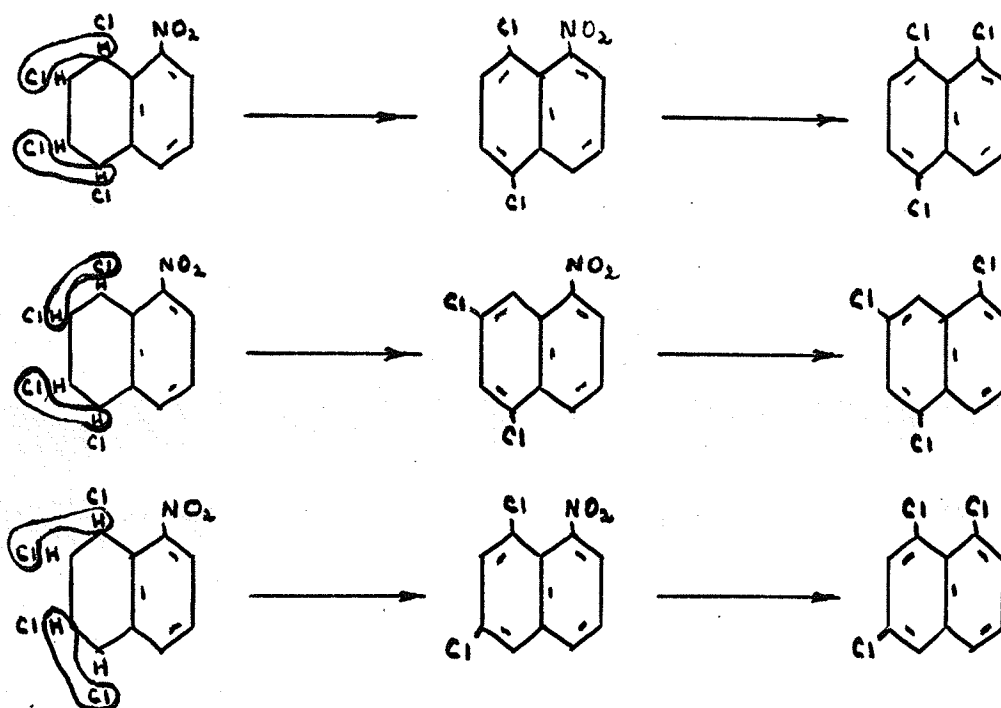
The nitro group in the alpha position of one ring orients new substituents to the other ring. One mole of chlorine may form a dichloride by adding to the 5,6- or the 7,8-positions, the latter being preferred. Elimination of hydrogen chloride at a moderate temperature will give the 5- and 8-chloro-1-nitronaphthalenes respectively. Addition of two moles of

chlorine will similarly form the 5,6,7,8-tetrachloride, which, on elimination of two moles of hydrogen chloride, will give 5,8-dichloro-1-nitronaphthalene (1,4-dichloro-5-nitronaphthalene):



If, however, the addition compound is heated, as in distillation, the subsequent decomposition of the dichloride or tetrachloride takes a different course. Apparently two reactions take place simultaneously. Hydrogen chloride is eliminated from the addition compounds, but the chloride atom may come from either the α or the β position, in contrast to being restricted to coming from the β position when the addition compound is not heated. At the same time, excess chlorine attacks the nitro group, eliminating it, or replacing it with chlorine. Other examples of halogens eliminating the nitro group or replacing it have been described by Cleve (24) and by Dhar (26).





The formation of 1-chloronaphthalene in the chlorination of 1-nitronaphthalene may be brought about by one of two possible mechanisms. The simpler one would be that chlorine attacks and replaces the nitro group without causing further substitution in the nucleus. The alternative might be that the 5- or 8-chloro-1-nitronaphthalene formed has its nitro group eliminated without replacement by chlorine, giving rise to this product.

The replacement of the nitro group by chlorine has also been accomplished using other chlorinating agents. For example, Atterberg (8) has described the conversion of 1,4-dichloro-5-nitronaphthalene to 1,4,5-trichloronaphthalene, using phosphorus pentachloride. Similarly, Vorozhtsov and Koslov (77) have reported the preparation of 1,8-dichloronaphthalene by the action of phosphorus pentachloride on 8-chloro-1-nitronaphthalene.

In spite of the fact that 8-chloro-1-nitronaphthalene is far more abundant than the corresponding 5-chloro- isomer when the reaction mixture is not heated, no 1,8-dichloronaphthalene has been obtained by the direct chlorination of 1-nitronaphthalene. This is accounted for by the rearrangement of 1,8-dichloronaphthalene to the 1,5- isomer. This rearrangement has been reported by Armstrong (5) who heated 1,8-dichloronaphthalene (melting at 89°) with concentrated hydrochloric acid in a sealed tube at 290° , obtaining 1,5-dichloronaphthalene (melting at 107°).

The presence of naphthalene in the chlorinated mixture may be accounted for by the nitro group being displaced from 1-nitronaphthalene without replacement by chlorine. It is also possible that naphthalene was present as an impurity in the 1-nitronaphthalene used by Buffle and Corbaz (19), since they used a technical grade of this reagent in their investigations.

The two tetrachloro- products obtained from the chlorination of 1-nitronaphthalene require only an extension of the above mechanism to account for their formation. The 1-nitronaphthalene-5,6,7,8-tetrachloride, or the related 5,8-dichloro-1-nitronaphthalene, is attacked by an additional two molecules of chlorine, which produce substitution in the 6 and 7 positions, to give the reported nitro-tetrachloronaphthalene, to which the structure 1-nitro-5,6,7,8-tetrachloronaphthalene is now assigned.

The reported tetrachloronaphthalene has a melting point in agreement with that for 1,2,3,4-tetrachloronaphthalene, which has been prepared by treating 1,1,2,3,4,4-hexachloro-

tetralin, or the dibromide of 5,6,7,8-tetrachlorotetralin, with alcoholic sodium ethoxide. The formation of this product in the chlorination of 1-nitronaphthalene may take place by elimination of the nitro group from 1-nitro-5,6,7,8-tetrachloronaphthalene without replacement by chlorine.

The above mechanism for the chlorination of 1-nitronaphthalene thus represents a development of the previously proposed mechanisms, and suggests in detail the steps involved in the formation of the products obtained experimentally. It is also consistent with theories proposed for the chlorination of naphthalene.

The establishing of the structures of the 1,3,5- and 1,3,8-trichloronaphthalenes, and the indication of the probable structures of the tetrachloronaphthalene and the nitrotetrachloronaphthalene, obtained from the chlorination of 1-nitronaphthalene, serve to contradict the statement of Ferrero and Wunenberger (34) that halogen can be introduced into the **B** position in naphthalene only by indirect means.

B Chlorination of 1-nitronaphthalene.

In connection with the present investigations, it appears that the preparation of 8-chloro-1-nitronaphthalene through chlorination of 1-nitronaphthalene, requires certain precautions, in order that the desired product may be obtained in a satisfactory yield and degree of purity.

The method of Ullmann and Consonno (72) can be improved by taking special care in some apparently small experimental details. The temperature of the reaction mixture during the chlorination should not be much above 60°. Thorough washing of the chlorinated mixture with warm water, and slow crystallization, facilitate the separation of the desired product from the undesired oily material by filtration and pressing. Recrystallization from benzene-ligroin proves far superior to recrystallization from alcohol, the oily impurities being quite soluble in ligroin, while the desired product is sparingly soluble at room temperature.

It may be noted that thorough washing with water removes any uncombined chlorine from the reaction mixture. This will account for the considerable amount of 1-nitronaphthalene recovered by distillation of the oily filtrate which remained after filtering off the 8-chloro-1-nitronaphthalene. The fact that the first signs of decomposition in the distillation of this residual oil occurred at a temperature above 190°, as compared with the decomposition temperature of 100-105° reported by Buffle and Corbaz (14) may also be accounted for by the absence of free chlorine in the mixture.

The isolation of the material melting at 32-34° through

cooling of an alcoholic solution of the chlorination mixture seems rather unusual. The constancy of the melting point on repeated recrystallizations from alcohol would seem to indicate purity, while all other evidence contradicts this. The chlorine analyses seem to indicate that the product might be a dimer or a double compound of 1-nitronaphthalene with a chloronitronaphthalene. However the molecular weight determination indicated that the product is a monomer in size. Crystallization of the product from ligroin, or from benzene-ligroin mixtures, gives a different melting point, which establishes that this low melting material is actually a mixture. The exact nature of the product can be elucidated only be Phase Rule studies on 1-nitronaphthalene and the chloronitronaphthalenes. Asacka (6) has reported a study of the three binary systems involving 4-, 5-, and 8-chloro-1-nitronaphthalenes, but no studies of the systems formed with these compounds and 1-nitronaphthalene have been reported.

The attempted chlorination of 1-nitronaphthalene in carbon tetrachloride solution at room temperature gives no chlorinated product, while no pure material could be isolated from the chlorination carried out in a boiling solution.

C Bromination of 1-nitronaphthalene.

The bromination of 1-nitronaphthalene in boiling carbon tetrachloride for the preparation of 5-bromo-1-nitronaphthalene presents no improvement over bromination of the fused 1-nitronaphthalene in the presence of iron powder or ferric

chloride, since this latter method is simpler experimentally, and gives higher yields.

The fact that the 5-bromo- product is obtained almost exclusively by bromination of 1-nitronaphthalene presents an interesting contrast to the diversity of the products obtained through the chlorination of the same compound. This is partially accounted for by the decreased reactivity of bromine as compared with the reactivity of chlorine under similar conditions. However, Dhar (26) has shown that bromine will attack 1,5- and 1,8-dinitronaphthalene to form 1,4,5,8-tetrabromonaphthalene by replacement of the nitro groups.

The reason for substitution taking place in the 5- position rather than in the 8- position is not clear, but McLeish and Campbell (55) have suggested one explanation. They propose that 8-bromo-1-nitronaphthalene is formed first. This, in the presence of hydrogen bromide, undergoes an isomeric change to 5-bromo-1-nitronaphthalene, in the same way that Armstrong and Wynne (5) have reported the conversion of 1,8-dichloronaphthalene to 1,5-dichloronaphthalene by the action of hydrochloric acid. An attempt to verify this idea by treating 8-bromo-1-nitronaphthalene with hydrobromic acid or bromine would be interesting.

D Nitration of 1-nitronaphthalene.

The nitration of 1-nitronaphthalene, and the separation

of the isomers by methods given in the literature has presented more difficulty than was expected. It seems that the chief difficulty lies in obtaining complete reduction of the 1,5-dinitronaphthalene to 5-nitro-1-naphthylamine without reduction of the 1,8-isomer. It is probable that the products obtained by the method of Hodgson and Walker (46), melting at 150-155°, and that obtained by the method of Gallotti and Galimberti (38) melting at 155-161°, were slightly impure 1,8-dinitronaphthalene, since Hodgson and Ward (47) give a setting point of 152° for a mixture containing 90% of the 1,8- isomer and 10% of the 1,5-isomer.

The preparation of 1,8-dinitronaphthalene through the action of nitrogen dioxide on naphthalene in solution, according to the method of Zakharov (81) presents some interest, as it apparently gives the desired product in better yields than those obtained by nitration of 1-nitronaphthalene, without requiring separation of isomers.

E Preparation of 1,8-dihalonaphthalenes.

The reduction of 8-chloro-1-nitronaphthalene to 8-chloro-1-naphthylamine according to the method of Adams and Steele (1) and the conversion of the amine to 1,8-dichloronaphthalene by a slight modification of the method of Bergmann and Hirshberg (15) proceeded satisfactorily. The preparation of 1-bromo-8-chloronaphthalene by the method of Feiser and Seligman (32) presented several difficulties. The method of diazotiz-

ation of the amine was satisfactory. However some changes have been made in the preparation of the cuprous bromide solution, in the coupling reaction, and in the purification of the product.

The literature method called for the use of dry cuprous bromide, excess sodium bromide, and copper, in suspension in hydrobromic acid. On warming to 75° to decompose the diazonium complex, the evolution of nitrogen proceeded very slowly with much tar formation, which caused difficulties in the subsequent purification, and consequent decrease in yield.

The alternative method used was to prepare the cuprous bromide solution directly from copper sulphate, and add the diazotized solution of the amine to this boiling cuprous bromide solution. Steam distillation of the bromo-chloronaphthalene, followed by trituration with sodium hydroxide and vacuum distillation, gave a product which was pure after one recrystallization from alcohol. The steam distillation was found to be preferable to the literature method of washing the product in ethereal solution with acid and alkali.

The yields obtained were lower than those reported for 1-bromo-8-chloronaphthalene by Feiser and Seligman, but the pure product was obtained more readily.

F Attempted preparation of 1,8-dimethylnaphthalene.

The preparation of 1,8-dimethylnaphthalene by Grignard reactions on 1,8-dihalonaphthalenes presents several difficulties. In almost all cases, the Grignard reaction proceeds slowly, and the reagent formed is slightly soluble in ether.

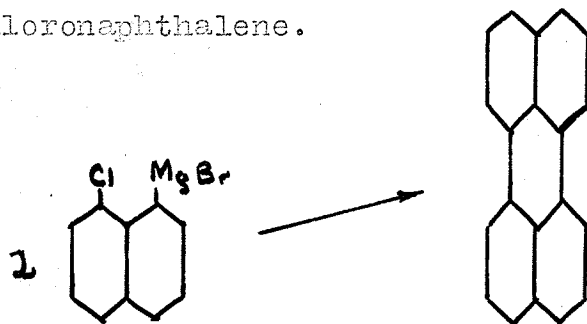
Feiser and Seligman (32) have studied the Grignard reactions of 8-bromo-1-iodonaphthalene and 1-bromo-8-chloronaphthalene with one mole of magnesium, and have prepared 8-bromo-1-methylnaphthalene and 8-chloro-1-methylnaphthalene by methylation of the corresponding Grignard reagents with methyl sulphate or methyl iodide. They have also reported that if the reaction of magnesium with the bromo-iodo compound is allowed to proceed rapidly, the product after methylation contains 1,8-dimethylnaphthalene and unchanged bromo-iodonaphthalene.

This is essentially the method used by Vesely and Stursa (74), who prepared 8-bromo-1-methylnaphthalene by a different method, and reacted this compound with methyl magnesium iodide and methyl sulphate to obtain the reported 1,8-dimethylnaphthalene. Thus it seems that 8-bromo-1-iodonaphthalene and 8-bromo-1-methylnaphthalene are the only naphthalene compounds which have been reported to give the 1,8-dimethylnaphthalene through methylation of the Grignard reagent.

All other Grignard reactions on 1,8-dihalonaphthalenes thus far studied have presented considerable difficulties. Feiser and Seligman (32) found that the reaction of magnesium with 1-bromo-8-chloronaphthalene proceeded quite slowly, att-

acking the bromine atom but not the chlorine atom. Methylation gave 8-chloro-1-methylnaphthalene, which in turn gave very little reaction with magnesium to form an insoluble Grignard reagent. 1,8-Dibromonaphthalene reacted similarly with magnesium to form an insoluble Grignard reagent. Willstaedt and Scheiber (30) reported the same result for the reaction of magnesium on 8-chloro-1-iodonaphthalene, while the same result was obtained for 1,8-dichloronaphthalene in the present work.

In the present investigations of Grignard reactions on 1-bromo-8-chloronaphthalene, products were obtained which were different from the starting materials, but no pure products have been isolated. The treatment of the Grignard reagent from this compound with methyl iodide gave a fluorescent solid which contained bromine, but was not pure. This was probably unchanged 1-bromo-8-chloronaphthalene together with a small amount of perylene, which is fluorescent. This compound could be formed by the reaction of the Grignard reagent with 1-bromo-8-chloronaphthalene.



On the other hand, methylation of the Grignard reagent with methyl sulphate gave an oily product, which was not further identified. The boiling point range of this oil seemed to be below that for either 1,8-dimethylnaphthalene or 8-chloro-1-methylnaphthalene. A further investigation of

this product might, however, indicate the presence of 1,8-dimethylnaphthalene, since Vesely and Stursa (74) have also obtained this product as an oil which would not solidify at -20° .

A study of the action of magnesium on the other halo-naphthalenes would be of interest, especially in the case of 1,8-di-iodonaphthalene, which might be expected to give a Grignard reaction more readily.

In the present study:

1. A complete description of a new, rather distinctive

product has been obtained which showed a typical benzene ring

fragments and a new (17) and (18) (74). The structure proposed

involved is that, when a certain kind of light is shined through

water through a small amount of a colored substance

which, in the case of 1,8-di-iodonaphthalene, is the

product, and may be converted to a new compound, the

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X-RAY POWDER PHOTOGRAPHS.

The technique of X-ray powder diffraction is one which has been extensively applied to inorganic chemistry and mineralogy, but which has had, thus far, little application in the field of organic chemistry. Since the equipment necessary for such an investigation is available in the Geology Department of the University of Manitoba, X-ray powder photographs were taken of the organic compounds used and prepared in the present studies.

A complete description of X-ray powder diffraction methods may be obtained from several standard texts, such as Bragg and Bragg (17), and Bunn (20). The essential principle involved is that, when a narrow beam of monochromatic X-rays passes through a small specimen of a powdered crystalline solid, numerous cones of diffracted beams emerge from the specimen, and may be recorded as arcs on a cylindrical strip of film mounted concentrically with the specimen. Each arc on the film represents the beam reflected from a particular set of planes in the crystal lattice. The position of each arc is determined by the spacing of the set(s) of planes reflecting it, and the intensity principally by the kind and arrangement of the constituent atoms. Since the lattice spacings and the kind and arrangement of the atoms are distinctive for any chemical compound, each will give its own characteristic powder photograph.

In tabulating the powder data of a substance, both the intensity and the position of each line are used. In conformity with present day usage, the intensities given in this

report are estimated visually, using a scale in which the strongest line on each film is arbitrarily assigned the value 10. It is customary to record the spacings of the lattice planes contributing to the lines, rather than the line positions on the film, since the latter vary with the wavelength of the X-rays and the diameter of the camera.

The powder cameras used in this investigation are of a diameter (57.3 mm.) such that a distance of 1 mm. on the film is equal to a Bragg angle of 1° . Thus the glancing angle θ for any lattice plane can be read from the film as one half the distance in mm. between the two corresponding arcs on the film. The glancing angle may be converted readily to the lattice spacing d of the corresponding lattice planes by a solution of the Bragg equation: $d = \lambda / 2 \sin \theta$, where λ is the wavelength of the X-rays. Fe radiation (Mn filter) was used for all photographs, and a set of lattice spacing tables for Fe $K\alpha_1$ Radiation by Beatty (14), based on the above equation, were used to convert the glancing angles to lattice spacings. All results are given in Angstrom units (Fe $K\alpha_1 = 1.936 \text{ \AA}$.)

Of the organic compounds studied in the present investigation, 1,8-dinitronaphthalene is the only one on which any X-ray data have been reported. Zhdanov and Umanskii (82) have reported from Laue photographs that 1,8-dinitronaphthalene crystallized in the orthorhombic system, having the cell dimensions: $a = 11.39$, $b = 15.15$, $c = 5.40 \text{ \AA}$. The unit cell contains four molecules; the calculated density is 1.53, and the observed density 1.46. The space group is given as

D₂⁴-P₂₁²₁²₁. No attempt was made to co-relate these cell dimensions with the present powder spacings.

X-ray powder photographs (Fe/Mn) were taken of the following compounds:

- (1) 1-nitronaphthalene-pure commercial sample.
- (2) 1,8-dinitronaphthalene -prep'd as on page **43**.
- (3) 5-bromo-1-nitronaphthalene -prep'd as on page **41**.
- (4) 8-chloro-1-nitronaphthalene -prep'd as on page **25**.
- (5) 8-chloro-1-naphthylamine -prep'd as on page **26**.
- (6) 1,8-dichloronaphthalene - prep'd as on page **29**.
- (7) 1-bromo-8-chloronaphthalene -prep'd as on page **27**.

TABLE I

OBSERVED X-RAY POWDER DATA

(1)) 1-Nitronaphthalene

$\frac{I}{d}$	$\frac{d}{\text{\AA}}$	$\frac{I}{d}$	$\frac{d}{\text{\AA}}$	$\frac{I}{d}$	$\frac{d}{\text{\AA}}$
5	10.29	4	3.52	2	2.38
8	8.00	9	3.33	1	2.24
5	6.82	3	3.21	2	1.999
10	6.22	1	3.09	1	1.932
5	5.17	3	2.89	1	1.898
4	4.18	1	2.73	1	1.849
4	3.99	2	2.65	1	1.772
4	3.84	1	2.59	1	1.675
6	3.71	1	2.54	1	1.264
7	3.61	1	2.48		

(2) 1,8-Dinitronaphthalene

$\frac{I}{d}$	$\frac{d}{\text{\AA}}$	$\frac{I}{d}$	$\frac{d}{\text{\AA}}$	$\frac{I}{d}$	$\frac{d}{\text{\AA}}$
1	8.24	7	2.80	2	1.774
3	7.57	4	2.66	2	1.742
7	6.25	1	2.56	2	1.694
9	5.71	5	2.48	1	1.645
1	5.31	1	2.45	1	1.614
2	5.10	2	2.38	1	1.536
2	4.86	1	2.33	1	1.523
7	4.64	4	2.26	1	1.489
3	4.10	2	2.11	1	1.415
2	3.92	2	2.07	1	1.373
10	3.79	2	2.01	1	1.325
5	3.48	4	1.938	1	1.286
8	3.04	4	1.887	1	1.199
7	2.85	1	1.833		

(3) 5-Bromo-1-nitronaphthalene

$\frac{I}{d}$	$\frac{d}{\text{\AA}}$	$\frac{I}{d}$	$\frac{d}{\text{\AA}}$	$\frac{I}{d}$	$\frac{d}{\text{\AA}}$
4	7.41	3	2.76	4	1.847
1	6.32	5	2.62	3	1.758
10	5.74	5	2.56	3	1.709
4	5.10	6	2.47	3	1.671
5	3.92	4	2.33	3	1.613
9	3.69	5	2.29	2	1.509
2	3.49	5	2.19	2	1.364
8	3.39	1	2.10	4	1.267
8	3.31	1	2.04	1	1.239
7	3.22	5	1.996	2	1.165
1	2.99	3	1.953		
5	2.86	3	1.907		

(5) 8-Chloro-1-nitronaphthalene

<u>I</u>	<u>d</u>	<u>I</u>	<u>d</u>	<u>I</u>	<u>d</u>
10	7.28	9	3.31	4	2.62
9	5.29	1	3.23	5	2.47
1	4.92	1	3.18	4	2.17
1	4.18	2	3.10	1	2.09
1	4.00	1	3.04	1	2.04
1	3.80	1	2.94	2	1.974
9	3.64	1	2.85	1	1.836
7	3.57	3	2.81	1	1.585
1	3.48	1	2.74	2	1.405
1	3.37	1	2.68		

(5) 8-Chloro-1-naphthylamine

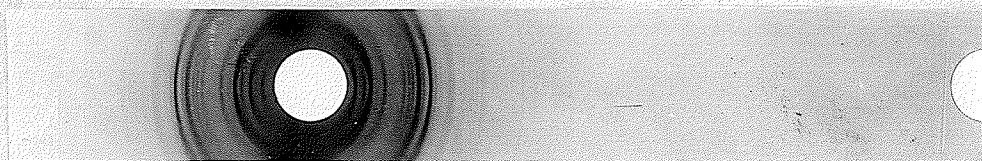
<u>I</u>	<u>d</u>	<u>I</u>	<u>d</u>	<u>I</u>	<u>d</u>
7	8.18	1	3.34	2	2.38
8	7.31	1	3.19	1	2.31
6	6.43	7	3.08	1	2.22
10	6.11	1	2.85	1	2.11
4	4.03	1	2.75	2	2.04
9	3.85	3	2.64	1	1.873
5	3.72	1	2.55		
9	3.47	2	2.44		

(6) 1,8-Dichloronaphthalene

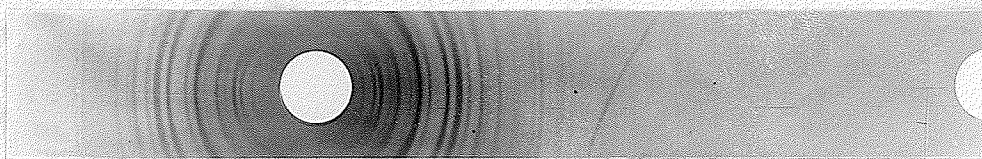
<u>I</u>	<u>d</u>	<u>I</u>	<u>d</u>	<u>I</u>	<u>d</u>
8	7.47	1	3.21	1	2.22
5	6.08	5	3.04	1	2.02
4	5.19	2	2.95	1	1.892
6	4.76	1	2.78	1	1.854
10	3.73	1	2.66	1	1.780
7	3.50	2	2.51	1	1.715
2	3.36	1	2.38		

(7) 1-Bromo-8-chloronaphthalene

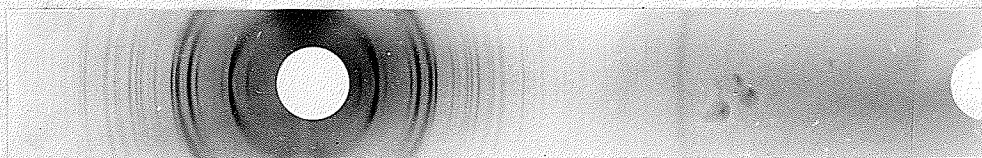
<u>I</u>	<u>d</u>	<u>I</u>	<u>d</u>	<u>I</u>	<u>d</u>
7	7.57	1	3.38	3	2.55
8	6.15	1	3.25	1	2.40
6	5.19	5	3.13	1	2.29
7	4.77	5	3.04	1	2.24
10	3.78	1	2.97	1	2.05
6	3.59	3	2.80	1	1.898
6	3.48	3	2.70		



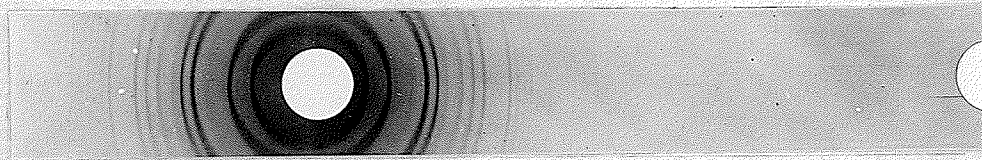
(1) 1-Nitronaphthalene



(2) 1,8-Dinitronaphthalene



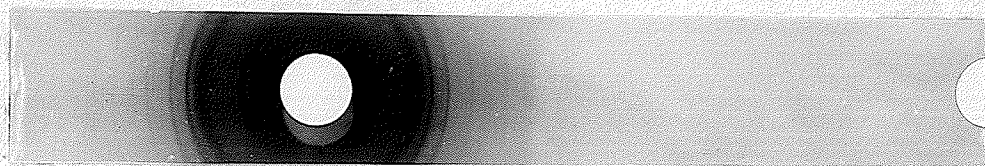
(3) 5-Bromo-1-nitronaphthalene



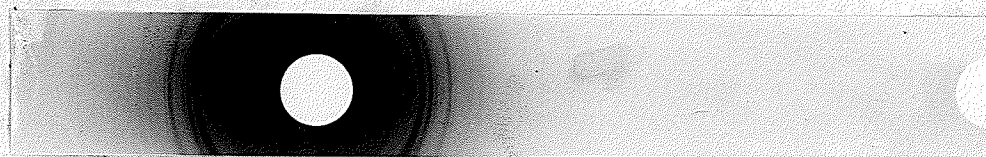
(4) 8-Chloro-1-nitronaphthalene

Figures 1-4: X-ray powder photographs, Fe/lin.

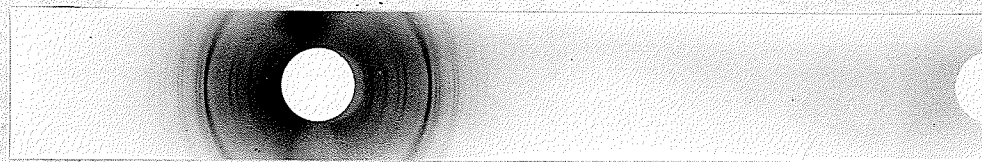
1 mm. on photograph: 1° .



(5) 8-Chloro-1-naphthylamine.



(6) 1,8-Dichloronaphthalene



(7) 1-Bromo-8-chloronaphthalene

Figures 5-7: X-ray powder photographs, Fe/Mn.

1 mm. on photograph = 1° .

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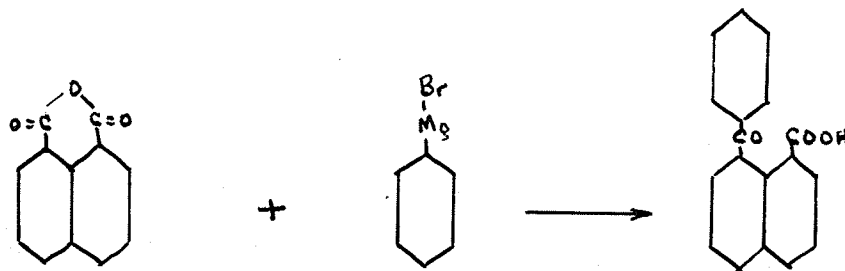
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PART IIGRIGNARD REACTIONS ON NAPHTHALIC ANHYDRIDEGENERAL SUMMARY

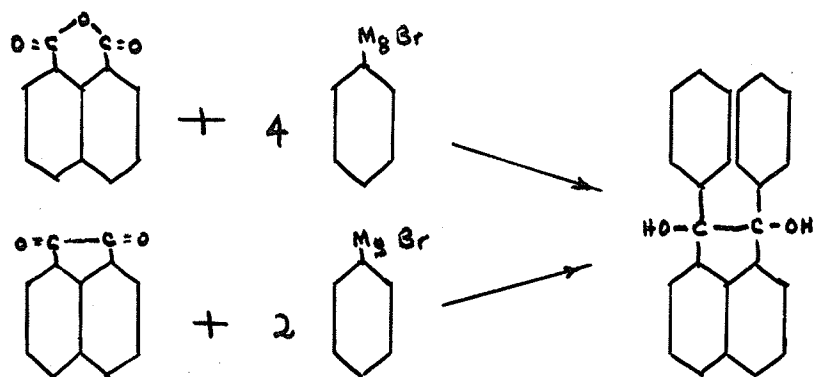
The action of Grignard reagents on naphthalic anhydride presents a method of obtaining various substituents in the 1,8- positions in naphthalene. A study of the literature indicates that this reaction has not been extensively studied, but that there seem to be two variations, leading to two general types of products.

In the one case, reaction of naphthalic anhydride with one mole of an aryl Grignard reagent (eg. phenyl magnesium bromide) leads to the formation of a ketonic acid, (eg. 8-benzoyl-1-naphthoic acid).



Alternatively, reaction of naphthalic anhydride with an excess (more than four moles) of the Grignard reagent results in the formation of an acenaphthene derivative (eg. 1,2-diphenyl-acenaphthenediol-1,2 from phenyl magnesium bromide). In this case, the addition of two moles of phenyl magnesium bromide is accompanied by a reduction which removes the oxygen bridge atom in the anhydride. The same products, and their stereoisomers, are also prepared from the reaction of

two moles of the Grignard reagent on acenaphthenequinone.



Various other aryl Grignard reagents have been used in reactions of the first type, while Grignard reactions on acenaphthenequinone have given numerous alkyl and aryl disubstituted acenaphthenediols. However the reactions of alkyl Grignard reagents on naphthalic anhydride have not been reported previously.

While no conclusive results have been obtained in the present investigations, due chiefly to the great difficulty encountered in removing impurities from the commercially available grade of naphthalic anhydride, the project presents some interest, and a survey of the work reported in the literature is herein presented. A description of the attempted reactions of the Grignard reagents from n-propyl bromide and n-butyl bromide on naphthalic anhydride is also included.

INTRODUCTION

Naphthalic anhydride and acenaphthenequinone are prepared by the oxidation of acenaphthene under various conditions. Oxidation of acenaphthene by dichromates in various solvents has been used by Gräbe and Gfeller (5), Jaubert (7), Duckert (4), Dashevskii and Karishin (3), and Ogilvie and Wilder (12), while oxidation in the vapor phase is the subject of patents by Jaeger (6). Whiston (14) has also reported a convenient oxidation of acenaphthenequinone to naphthalic anhydride by means of hydrogen peroxide.

For the purification of naphthalic anhydride, which is sparingly soluble in the usual solvents, Jaubert (7) suggested recrystallization from concentrated nitric acid, S.G. 1.48, reporting that the anhydride was stable in this solvent. However, Mihailescu and Steopoe (11) have shown that naphthalic anhydride in boiling nitric acid leads to the formation of 3-nitronaphthalic anhydride and a dinitro derivative. These authors suggested the use of glacial acetic acid for recrystallization.

In investigations of the reaction of one mole of a Grignard reagent with naphthalic anhydride, several different Grignard reagents have been used. Weiss and Fastmann (13) have used Grignard reagents from 1-bromonaphthalene, benzyl chloride, and o-tolyl bromide to obtain the corresponding 8-ketonic-1-naphthoic acids such as 8-(1'-naphthoyl)-1-naphthoic acid.

Knapp (8) has used phenyl magnesium bromide and 2-methoxy-1-naphthalene magnesium bromide in a similar manner.

For the alternate Grignard reaction using an excess of the Grignard reagent on naphthalic anhydride, Wittig, Leo, and Weimer (15) have used phenyl magnesium bromide, and have obtained 1,2-diphenyl-acenaphthenediol-1,2. Beschke (2) and others have prepared this same product by the action of two moles of phenyl magnesium bromide on acenaphthenequinone. Grignard reactions with other aryl and alkyl halides have been carried out on acenaphthenequinone, to give products of analogous structure. Of special interest in connection with the present investigation is the work of Maxim (9). This author used Grignard reagents from methyl iodide, ethyl bromide, propyl iodide, isobutyl bromide, and isoamyl bromide, which gave the corresponding 1,2-dialkyl-acenaphthenediol-1,2. on reaction with acenaphthenequinone.

It seems probable that the same products would result from the treatment of naphthalic anhydride with excess of the corresponding alkyl Grignard reagents. An attempt has been made to carry out this reaction with n-butyl bromide and n-propyl bromide, but the expected products have not been isolated.

EXPERIMENTAL WORK

The practical grade of naphthalic anhydride (Eastman) available was reddish in color, and melted at 245-253°, in contrast to the white color and melting point of 274° reported for the pure material. An attempt was therefore made to purify this material according to the methods found in the literature.

Purification of naphthalic anhydride

The crude naphthalic anhydride (50 gm.) was dissolved in large volumes of hot sodium hydroxide solution, the undissolved material being filtered off on a sintered glass Buchner funnel. The hot filtrate was carefully acidified with concentrated hydrochloric acid, giving a bulky brown precipitate of the anhydride, which was collected by filtration.

This partially purified material was repeatedly recrystallized from hot glacial acetic acid, decolorizing with charcoal. The final product obtained was in the form of tan colored plates (10 gm.) melting at 272-275°. The literature melting point is 274°.

Grignard Reactions

(1) Action of n-butyl bromide on naphthalic anhydride.

The Grignard reagent was prepared from n-butyl bromide (2.7 cc.; 0.025 moles) and magnesium (0.61 gm.) in absolute ether (10 cc.). To this was added a suspension of purified

naphthalic anhydride (1.0 gm., 0.005 mole) in absolute ether (100 cc.). The ethereal solution became very dark in color, while much of the anhydride settled out. The solution was refluxed for several hours, and was then poured into a mixture of dilute sulphuric acid and ice to decompose the Grignard complex. The ethereal solution was separated, and allowed to evaporate. The crystalline material which settled out first melted at about 265° , and was therefore impure naphthalic anhydride. Complete evaporation of the ethereal solution gave a reddish brown resinous material, which could not be further purified. This resin was soluble in acetone and in alcohol, and was therefore different from naphthalic anhydride.

(2) Action of n-propyl bromide on naphthalic anhydride.

The Grignard reagent was prepared from n-propyl bromide (2.3 cc., 0.025 mole) and magnesium (0.61 gm.) in absolute ether (10 cc.). A suspension of naphthalic anhydride (1.0 gm.) in absolute ether (60 cc.) was added to the Grignard reagent. Some boiling of the ether occurred during the addition of the naphthalic anhydride. The solution was then refluxed for four hours.

Decomposition of the Grignard complex with dilute sulphuric acid, and evaporation of the ether solution, gave a resinous product. This was partially dissolved in alcohol (30 cc.) leaving an insoluble residue (0.11 gm.) of naphthalic anhydride melting at $267-272^{\circ}$ with decomposition.

Evaporation of the alcoholic solution gave a dark brown resin, from which none of the expected 1,2-dipropyl-acenaphthenediol-1,2 melting at 173° could be isolated. This product was obtained by Maxim (9) through the action of the Grignard reagent from n-propyl iodide on acenaphthenequinone.

DISCUSSION

One of the chief difficulties encountered in the study of the reactions of Grignard Reagents on naphthalic anhydride seems to be the purification of the naphthalic anhydride used as a starting material. This purification is necessary, since otherwise the resinous impurities prevent purification of the final product.

An alternative to purifying the commercial naphthalic anhydride might be the preparation of acenaphthenequinone according to the method of Maxwell and Allen (10), and oxidation with hydrogen peroxide according to the method of Whiston (14), to give purified naphthalic anhydride.

The preparation of 1,2-diphenyl-acenaphthenediol-1,2 according to the method of Wittig (15) has been reported by Bartlett and Brown (1) to present difficulties. These authors found the Grignard reaction on acenaphthenequinone to be far more successful. It would therefore seem that this latter method would be more suitable for the preparation of substituted acenaphthenediols. However, the formation of the C-C bond by reduction during the Grignard reaction on naphthalic

anhydride presents some interest from a theoretical viewpoint, since a di-tertiary alcohol would be the expected product.

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CONCLUSIONS.

1. A survey of the literature dealing with the reported preparations of 1,8-dimethylnaphthalene has been presented.
2. A thorough study of the various methods of preparing 1,8-dihalonaphthalenes from available materials has been made.
3. All the reported products obtained from the chlorination of 1-nitronaphthalene have been tabulated, and a mechanism to account for their formation has been proposed. The probable orientations of the substituents in two of these products, the tetrachloronaphthalene and the tetrachloro-nitronaphthalene, have been suggested.
4. A number of attempts to prepare 1,8-dimethylnaphthalene by Grignard reactions on 1,8-dichloronaphthalene and 1-bromo-8-chloronaphthalene have proved unsuccessful.
5. The previously reported reactions of Grignard reagents on naphthalic anhydride, and two new attempted reactions of this type, have been described.
6. The X-ray powder diffraction photographs of seven naphthalene compounds have been taken, and the data obtained have been tabulated.