

The Sect.

Thesis for the Degree of Ph.D.

by

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"THE INFLUENCE OF THE NATURE AND POSITION OF
ATOMS IN ORGANIC COMPOUNDS ON THE REACTIVITY
OF THE OTHER ATOMS IN THE SAME MOLECULE".
THE NAPHTHALENE SERIES.

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Chemists have long been interested in the influence exerted by an atom on other atoms in the same organic molecule, the earliest suggestions on this subject being put forward by Markownikoff in 1870 (Annalen 153,256.)

Since then, many investigators have pursued research in the hope of discovering the nature of this mutual influence of atoms in an organic molecule, which makes itself apparent in many ways, such as ortho-para or meta substitution in a substituted benzene nucleus, differences in lability of halogen atoms in isomerides, tautomerism etc.

The usual formulae employed in organic chemistry do not represent or explain why differences should occur, and it has been the aim of some chemists to express the cause of such phenomena in a graphical manner and the suggestions of Thiele (Ann.,1899,306, 87), Vorländer, (Ann., 1902,320, 66) (J. pr. chemie, 1902, 66, 321; 1905, 71, 497; J. C. S., 1909, 95, 718; 1910, 97, 84.) Fry (J. Amer. Chem. Soc., 1912, 34, 664), Robinson (T. 1916 109, 1029; 1917, III, 958), Vorländer (Ber., 1919, 52, 263), and Lapworth (Mem. Manchester, Phil. Soc., 1920, 64, No. 3) are to be regarded as fundamental in this sense.

The theory propounded by Lapworth (loc.cit.) has created much interest. It involved a principle of/

of induced alternate polarity, and grouped together many otherwise disconnected facts e.g. substitution in benzene ring, α - γ reactivity in aliphatic compounds, tautomerism, addition of halogen acid to unsaturated aliphatic compounds etc.* It did not postulate the prime cause of the differences but Lapworth (J. C.S., 1922, 121, 416) and Robinson and Kermack (J.C.S., 1922, 121, 427,) showed how such differences could be caused, the latter especially stressing the stability of electron octets as being responsible for the reactivities observed.'

The views put forward by Lapworth in 1920 have been substantiated in many ways, particularly by investigations on the reactivity of the halogen atoms in a series of aromatic halogen compounds (Lapworth and Shoesmith J.C.S., 1922, 121, 1391; Shoesmith and collaborators J.C.S., 1923, 123, 2698 and 2828; 1924, 124, 1312 and 2279; 1926, 127, 214).

The investigations have so far been confined to the benzene series and the present work was carried out to discover the similarities which may or may not exist between benzene and naphthalene halogen compounds in their behaviour in the light of the original suggestions. Extraordinary interest attaches itself to an influence transmitted from one ring to the other and a number of halogen compounds have been prepared and the lability of the halogens investigated in order to see/

see

1. if the influence of a substituent on an atom in the same ring is similar to that, already discovered in the benzene series and

2. how far such influences are transmitted from one ring to another.

The classes of compounds examined were

1. Various bromo-naphthols to compare with the bromo-phenols.

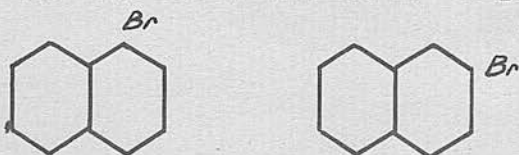
2. bromo-methyl-naphthalenes to compare with bromo-toluenes

3. α and β naphthyl methyl bromides to compare with benzyl bromide and

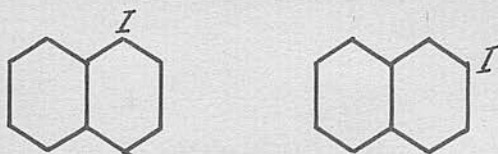
4. methoxy and -bromo-naphthyl-methyl bromides to compare with the methoxy- and bromo benzyl bromides.

The full list of compounds investigated is as follows:

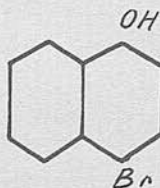
I. The two isomeric bromo-naphthalenes.



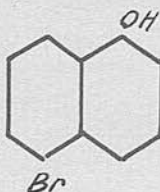
II. The two isomeric iodo-naphthalenes

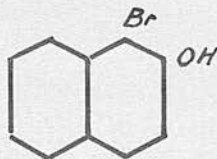
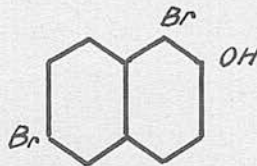
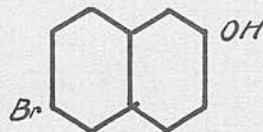
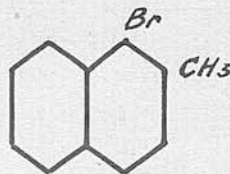
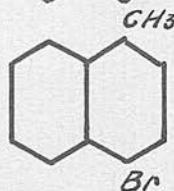
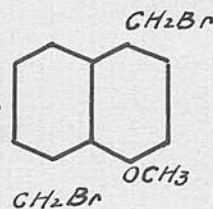
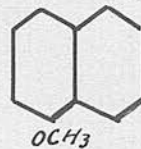
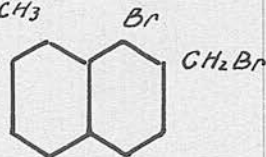
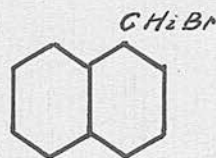
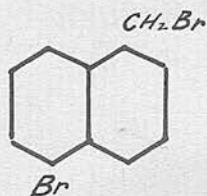


III. 4-Bromo- α -naphthol



5-Bromo- α -naphthol



I-Bromo- β -naphtholI-6-dibromo- β -naphthol6-Bromo- β -naphthol
(not isolated)IV. I-Bromo- β -methyl naphthalene4-Bromo- α -methyl naphthaleneV. α and β -naphthyl methyl bromide $C_{10}H_7CH_2Br$ VI. 4-methoxy- α -naphthyl methyl bromide5-methoxy- α -naphthyl methyl bromideVII. I-Bromo- β -naphthyl methyl bromide4-Bromo- α -naphthyl methyl bromide5-Bromo- α -naphthyl methyl bromide

Considerable difficulties were encountered throughout the whole research with regard to the preparation of some of these compounds. Although partly expected, they were due to the fact that comparatively little is known about this series of naphthalene derivatives and the yields of intermediate products are very low.

The two reagents used in this research were those already employed with great success in previous work, namely hydrogen iodide in aqueous acetic acid, and aqueous alcohol. Reactivities were investigated at various temperatures and the following observations were made.

The examination of the reactivity of mono-halogenated naphthalene derivatives showed that α -bromo- and α -iodo naphthalene are more readily reduced by hydriodic acid than the corresponding β compounds, as will be seen from the table on curves page 56 .

The iodo naphthalenes are more reactive than the bromo naphthalenes.

The order of ease with which the bromine of the bromo-naphthols examined, is removed is the following:

I-Bromo- β -naphthol $>$ 4-bromo- α -naphthol $>$ 5-bromo- α -naphthol. An important and very large difference exists between the latter, when the bromine atom is in/
in/

in a different ring from the hydroxyl group and the former two which behave similar to the corresponding bromo-phenols, excepting that they are much more readily reduced in the order 1:2 > 1:4, the reverse of the bromo and iodo phenols (curves II page 66).

1:6 dibromo- β -naphthol again is much less reactive than the 1-bromo- β -naphthol.

The action of hydro iodic acid on 1-bromo- β -methyl naphthalene and 4-bromo- α -methyl naphthalene showed that the bromine of the 1:2 compound is more readily removed than that of the 1:4 isomeride, which is in accordance with the order of reactivity of iodo toluenes. (figure ^{III} / page 67). It is note worthy that the bromo toluenes however are stable towards hydro iodic acid.

α and β naphthyl methyl bromides were submitted to the action of hydro iodic acid and also aqueous alcohol. With the former agent no marked difference was observed (fig IV page 68), the β compound being very slightly more reactive than the α derivative. The hydrolysis however showed the reverse order of reactivity and here \neq difference was marked. With both compounds the reactions were more rapid than with benzyl bromide. The comparison with the latter is given in figures ^{V and VI} / page. 69 & 70.

The order of ease with which the hydrolysis of 4-methoxy- α -naphthyl methyl bromide and 5-methoxy- α -naphthyl methyl bromide takes place is 4 > 5. There is /

is a very marked difference in the rate of hydrolysis between the $-\text{CH}_2\text{Br}$ in the first and the $-\text{CH}_2\text{Br}$ in the second ring. The 1:4 compound is very unstable and is hydrolysed almost at once. A similar fact was observed with p-methoxy benzyl bromide which is at once completely hydrolysed when brought into solution in aqueous alcohol.

In the case of the substituted naphthyl methyl bromides, such as:

1-bromo- β -naphthyl methyl bromide

4-bromo- α - " " "

5- " - α - " " "

the order of ease with which the bromides lost their bromine as bromide ion in solution in aqueous alcohol is $1:4 > 1:5 > 2:1$ and compared with the unsubstituted naphthyl methyl bromides; unsubstituted $>$ ~~unsubstituted~~.

The bromo naphthyl methyl bromides could not be submitted to the action of hydroiodic acid since in addition to the side chain bromine atom, that in the ring would have been removed by the reducing agent.

Thus a representative class of compounds in the naphthalene series has been examined. Experiments were also carried out to obtain,

1. 2-methoxy- α -naphthyl methyl bromide,

2. 3 " - α - " " " ,

3. 6 " - α - " " " /

4. 7 " - α - " " " /

but were /

were unsuccessful owing to the difficulties of obtaining sufficient quantities of methoxy naphthoic acids in the last three isomerides. As described in the preparative part, various methods were tried in order to obtain 2-methoxy- α -naphthyl methyl bromide. The failure of some of these is probably due to the steric influence of the methoxy group in ortho position.

The following pages give an account of the preparation of the following compounds.

- I. α - and β -Bromo naphthalenes
2. α - and β -Iodo naphthalenes
3. α - and β -naphthyl methyl bromides
4. 1-Bromo- β -naphthyl
5. 4-Bromo- α -naphthyl
6. 5-Bromo- α -naphthyl
7. α -Naphthyl carbinol
8. 2-Methoxy- α -naphthaldehyde
9. 2-Hydroxy- α -naphthyl carbinol
10. 4-Methoxy- α -naphthaldehyde
11. 4-Methoxy- α -naphthyl carbinol
12. 4-Methoxy- α -naphthyl methyl bromides
13. Attempts to prepare
 - 2-Methoxy- α -naphthyl carbinol and
 - 2-Methoxy- α -naphthyl methyl bromide
14. 3-Methoxy- α -naphthaldehyde
15. 3-Methoxy- α -naphthyl carbinol
16. 5-Methoxy- α -naphthaldehyde
- 17/

17. 5-Methoxy- α -naphthyl carbinol
18. 5-Methoxy- α -naphthyl methyl bromide
19. 6-Methoxy- α -naphthoic acid
20. 7-Methoxy- α -naphthoic acid
21. 1-Bromo- β -naphthyl methyl bromide
22. 4-Bromo- α - " " "
23. 5-Bromo- α -naphthaldehyde
24. 5-Bromo- α -naphthyl carbinol
25. 5-Bromo- α -naphthyl methyl bromide.

PREPARATIVE. β -Bromonaphthalene (Ann. 183, 268)

This naphthalene derivative was obtained from β -naphthylamine by means of a Sandmeyer reaction. The following proportions were used:

15 gms. β -naphthylamine
 140 c.c. hydrobromic acid (47%)
 100 c.c. water

This mixture was boiled until the solution was clear, cooled, diazotised in the usual way at 0° and then added to cuprous-bromide solution. The whole was then heated on a steam bath for one hour.

After steam distillation, β -bromonaphthalene was recrystallised from alcohol. m.p. 59°.

 α -Iodonaphthalene. (Ber., 1886, 19, 136.)

α -Diazonaphthalenesulphate was boiled with potassium iodide in an acid solution. Excess of hydro^oiodic acid is avoided, since slight reduction to naphthalene takes place.

α -Iodonaphthalene, a heavy oil of b.p. 306°, in a yield of 55%, was obtained by steam distillation of the whole.

 β -Iodonaphthalene (Ber., 1881, 14, 804)

As in the case of β -bromo-naphthalene, the corresponding iodo compound was obtained from β -naphthylamine/

β -naphthylamine which was first converted into the sulphate. Owing to its high insolubility it could be isolated in very pure condition, a fact, which influenced considerably the yields in a favourable manner. β -Naphthylamine sulphate (14 gms.) suspended in water, was diazotised with the theoretical quantities of acid and sodium nitrite (6 c.c. H_2SO_4 ; 4 gms $NaNO_2$) Hydro iodic acid (2 gms. per 1 gram of sulphate) of spec. gravity 1.7 was now added. Nitrogen was immediately evolved and a red precipitate produced. After heating for some time on a steam bath, the precipitate melted to a heavy black oil which solidified again on cooling. This residue was now extracted with alcohol, filtered and the filtrate diluted with water. Crystals precipitated after a short time and the compound was finally purified by several subsequent steam distillations. It had m.p. 54.5°

Naphthyl - 1- methyl bromide.

α -Methyl naphthalene was heated to 230° and whilst being stirred by a slow passage of a current of dry air an equal weight of bromine was gradually added during an interval of ten minutes. (Ber., 1916, 49, 2832) The stream of dry air was passed through the reaction product in order to remove any remaining hydrobromic acid. The product was distilled in vacuo, when about one fifth of the methylnaphthalene was recovered unchanged.

Naphthyl-1-methylbromide/

Naphthyl-1-methylbromide, b.p. $181^{\circ}/23$ m.m. was obtained first as a heavy oil, which solidified when cooled in a freezing mixture. Crystallisation from petrol ether yielded after a few repetitions a pure compound. (Both naphthyl methyl bromides are very lacrimatory.)
m.p. 52° .

Analyses: Found: Br, 35.95%

$C_{11}H_9Br$ requires Br, 36.44%.

Naphthyl-2-methyl bromide. (Ber., 1884, 17, 1529)

Bromine vapours are introduced in a current of carbon dioxide gas into β -methylnaphthalene maintained at 240° .

Naphthyl-2-methylbromide was isolated in a similar way to that described for the corresponding α /compound and crystallised from alcohol in large plates. m.p. 56° .

Analyses: Br found 36.15% $C_{11}H_9Br$ requires 36.24%.

The preparations of hydroxy and also methoxy-bromonaphthalenes were undertaken in order to obtain information:

a. about the influence of a hydroxy-group either in the same or in different rings on the bromine atom in I position, and

b. it was hoped, that the methoxy bromo-naphthalenes would give the methoxy naphthylbromides. The latter scheme was however abandoned for various reasons!

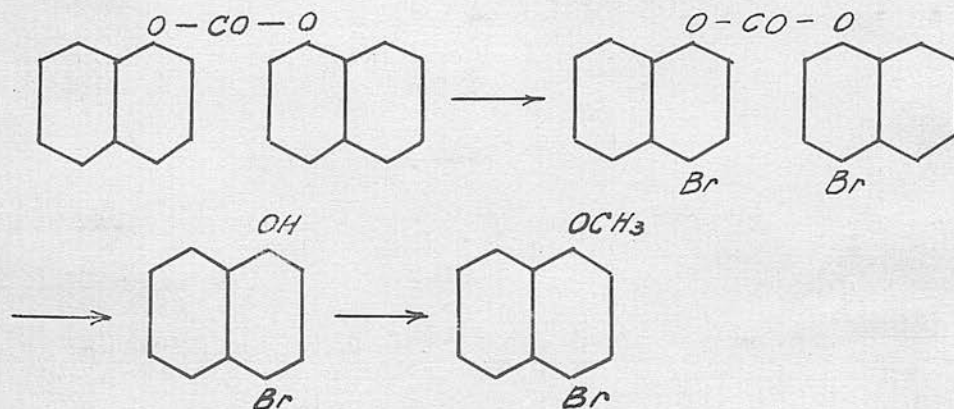
I-Bromo-2-methoxynaphthalene. (J.C.S. 1879, 35, 789)

β -Naphthol in moderately concentrated glacial acetic/

acetic acid solution was heated with the theoretical quantity of bromine, dissolved in approximately an equal volume of glacial acetic acid. The whole solution was cooled during this operation and the flask shaken after each addition of bromine, which is quickly absorbed. On standing, colourless needles were crystallise out, which are then washed from excess of acetic acid with water and dried. m.p. 84° from alcohol.

The corresponding methoxy compound was obtained by methylating I bromo-2-hydroxy naphthalene with excess of methylsulphate. m.p. 83° .

4 Bromo-I-methoxy naphthalene was prepared as follows:



α -Naphthyl-carbonate. (Ber., 1894, 27, 3459.)

Phosgene was passed for three hours into α -naphthol (100gms.) dissolved in a solution of 100 gms. of sodium hydroxide in 100 c.c. water, at ordinary temperature, when the α -naphthyl carbonate is precipitated.

The reaction is finished, when the alkaline solution is/

is free from naphthol. After filtering and washing, the compound may be crystallised from glacial acetic acid or benzene. M.p. 170° .

Bromination of α -naphthylcarbonate.

To a hot solution of 31 gms. α -naphthylcarbonate in 250 c.c. glacial acetic acid 12 c.c. of bromine in 50 c.c. acetic acid are rapidly added with continuous stirring. The bromo compound crystallises out from the hot mixture, is filtered off and washed with acetic acid.

It crystallises from a large quantity of benzene in needles of m.p. 214° .

4-bromo- α -naphthylcarbonate with alcoholic potassium hydroxide yields

4-bromo- α -naphthol. Kauffmann (Ber., 1895, 28, 3053) gives m.p. 127° , but when ^{steam} distilled in an atmosphere of nitrogen, the compound was obtained as colourless light needles of m.p. 129° .

During the course of these experiments 4-bromo-1-naphthol was observed to become very brown in the atmosphere. The methylation was therefore carried out in an atmosphere of nitrogen in order to avoid oxydation by the air. The operation was very difficult and the following precautions must be taken to avoid excess of tar.

In the presence of only a trace of unmethylated compound, the 4-bromo-1-^{methoxy naphthalene}~~naphthol~~ could not be distilled/

distilled. The bromo-naphthol in alkaline solution was shaken with excess of dimethylsulphate at ordinary temperature for several hours in an atmosphere of nitrogen. The ethereal extract of the acidified solution was then several times carefully washed with caustic soda and dried over calcium chloride.

After distillation in vacuo a yield corresponding to 20% of the calculated quantity of ether expected, was obtained.

The following method, which combines the hydrolyses of the bromocarbonate and the methylation of the resulting 4-bromo-I-naphthol in one operation was finally adopted.

In this way, the separation of the unstable 4-bromo-I-naphthol was avoided and hence air oxydation reduced to a minimum.

The bromocarbonate (20 gms.) was dissolved in methylalcoholic potassium hydroxide, (100 c.c. + 4.8 gms of KOH) and a slight excess of the theoretical quantities of dimethylsulphate and potassium hydroxide gradually added from two dropping funnels. The solution was then heated for about two hours on a steam bath. A stream of nitrogen gas was passed into the whole during the experiment. The solution was finally steam distilled and the light oil so obtained extracted with ether and washed with alkali.

With the aid of a Widmer vacuum distillation column (vide *Helv. chim. Acta* 1924, 7, 59) two fractions were/

were readily separated, namely:

- a. α -methoxynaphthalene $174^{\circ}/16\text{m.m.}$
 b. α -methoxy-4-bromonaphthalene
 179° (181°), 16 m.m. (18m.m.).

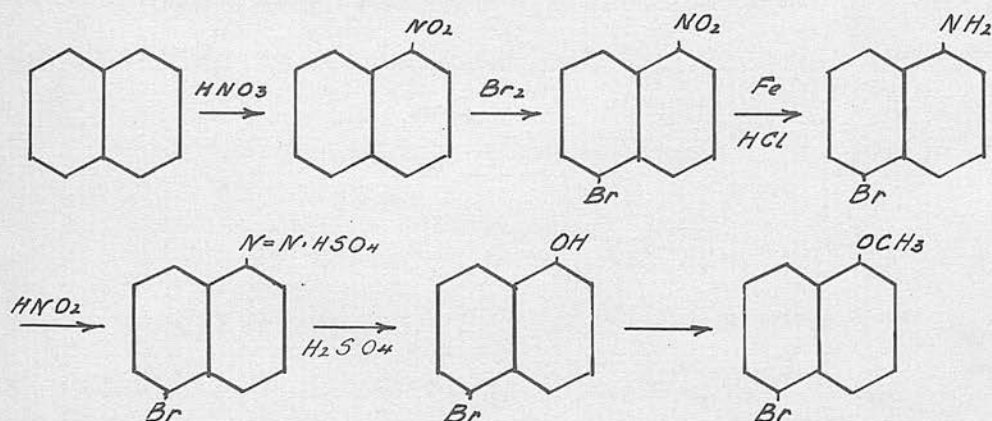
Yield 55%, calculated to bromo carbonate.

Analyses: Found: Br, 33.60%; $\text{C}_{11}\text{H}_9\text{OBr}$

requires: Br, 33.80%.

The small proportion of α methoxy-naphthalene present is due to some unbrominated naphthylcarbonate.

5-Bromo-1-methoxynaphthalene was prepared according to the following scheme



The nitration of naphthalene was carried out out in glacial acetic acid solution and the α -nitronaphthalene (m.p. 61°) converted by bromination into 5-bromo-1-nitronaphthalene (Ann., 1884, 222, 290).

Of the various methods tried, the following produced the best results: Bromine (40 gms.) was gradually/

gradually dropped into vigorously stirred, melted nitronaphthalene (85 gms.), the temperature being maintained between 80 and 100°. Care was taken, that the nitronaphthalene used was absolutely dry.

After one crystallisation from alcohol a substance of m.p. 122° was obtained and was found to be pure bromo-nitronaphthalene. Other methods yielded a mixture of 5-bromo-I-nitronaphthalene, unchanged nitronaphthalene and ^athird compound (m.p. 165°), probably a dibrominated nitro-naphthalene, the constitution of which was not ascertained.

Considerable difficulty was experienced in the reduction of the bromo-nitronaphthalene to the corresponding amino compound and the diazotation of the latter.

The methods employed were;

1. Reduction by means of SnCl_2 and HCl.

(Ber., 1902, 35, 2804)

2. Reduction by means of iron filings and HCl.

The latter yielded the best results and was therefore finally adopted.

^{For}
In comparative purposes details of the first method are given.

10 gms. of 5-bromo-I-nitronaphthalene were gradually added to a hot solution of 28 gms. stannous chloride in 40 c.c. conc. hydrochloric acid and 50 c.c. alcohol. The tin double salt was readily formed, was decomposed with sodium hydroxide, and the 5-bromo-

I-naphthylamine so formed extracted with ether, the ether evaporated away and the amino-compound separated from tar by crystallisation from ligroin. It formed blueish-red coloured crystals, m.p. 67° .

The amino-compound may also be purified by distillation in a current of steam. Yield: 25%.

Yields of 85% however have been obtained when iron filings and a small quantity of hydrochloric acid were used as reducing agents.

Iron filings (60 gms.) were added to 40 gms. 5-bromo-I-nitronaphthalene dissolved in 600 c.c. alcohol and 8 c.c. hydrochloric acid. After boiling the whole for 2 hours, the solution was made alkaline with alcoholic potassium hydroxide and filtered hot. The alcohol was then partly distilled away, when the amino-compound appeared as a dark substance, which was crystallised from ligroin. The residues were finally steam distilled.

The compound was then seen to be slightly coloured plates from ligroin, or needles when steam distilled of m.p. 69° , which become dark on exposure to the atmosphere.

The diazotation of 5-bromo-I-naphthylamine was carried out in 10% sulphuric acid; 10 gms. require about 1200 c.c. of acid. The sulphate is very insoluble and crystallises out immediately. Continuous stirring was therefore necessary during the operation. Less than the theoretical quantity of sodium nitrite was used in order to avoid tarring. The diazotation took/

took place very slowly and when all the nitrite was added the liquid was filtered to remove unchanged bromo-naphthylamine.

The diazocompound is very stable and evolves nitrogen only when heated on the steam bath.

The hydrolysis was found to be the most difficult stage of this synthesis on account of the ready formation of hydroxyazocompounds.

After many attempts, the method adopted was as follows:

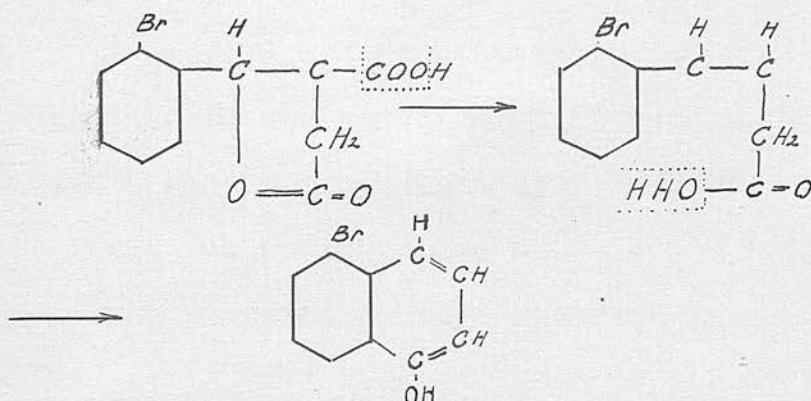
The solution of the diazotised amine was added slowly to a boiling solution of 33% sulphuric acid and the 5-bromo- α -naphthol distilled as white needles which had m.p. 137°.

Only 10% of the expected quantity was obtained because of the formation of much tar. The properties of 5-bromo-1-naphthol are similar to those of the corresponding 1:4 derivative, described on a previous page.

In order to confirm the 5 position of the bromine atom, a small sample was methylated and converted via the magnesium-compound into 1-methoxy-5-naphthoic acid. The m.p. found was 227° and ~~was~~ identical with that recorded by Royde and Schedler in J.C.S. 1923, 73, 1641, as the m.p. of 1-methoxy-5-naphthoic acid, which was prepared too in the course of this research by the present author.

5-Bromo-1-naphthol has been recently prepared by Fuson/

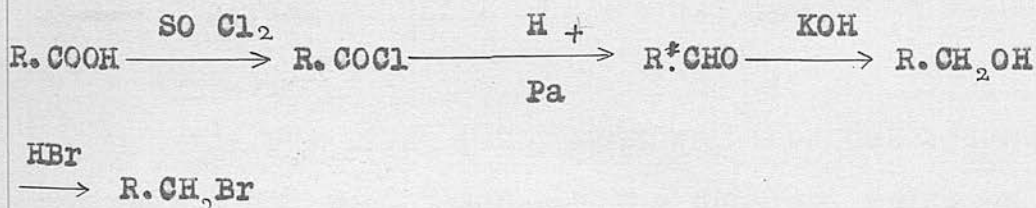
Fuson, J. Amer. Chem. Soc., 1924, 46, 2779, in a manner similar to the one outlined above and also as follows:



The compound described here possesses properties similar to those described by Fuson.

The following gives an account of preliminary experiments, undertaken with a view to obtain information about the methods of preparing isomeric methoxy-naphthyl-methylbromides.

It was hoped to obtain these by the following series of reactions:



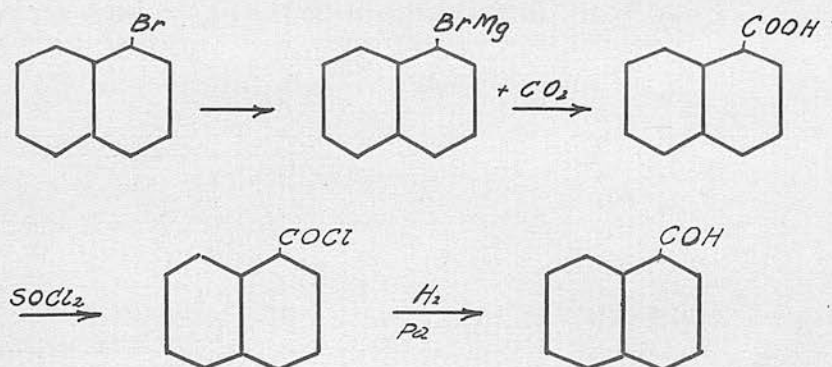
where R represents $\text{MeO} \cdot \text{C}_{10} \text{H}_6 -$.

(In some cases the aldehyde could be obtained by Gattermann's HCN methods (Ann. 1907, 357, 313) as is shown later). Therefore preliminary experiments were necessary/

necessary in order to discover to what extent the catalytic reduction above mentioned (see Rosenmund, Ber., 1918, 51, 585) could be employed in the naphthalene series.

Therefore, α -naphthoylchloride was prepared and submitted to the action of hydrogen in presence of palladinised barium sulphate.

The following scheme shows how α -naphthylaldehyde was prepared by such reaction.



α -Bromonaphthalene and magnesium in ethereal solution readily gave the intermediate compound, as shown, and the ethereal solution of this was saturated with carbon dioxide.

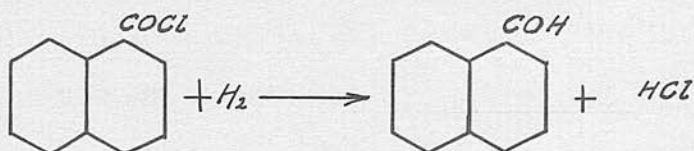
The resulting pasty mass was then decomposed with dilute sulphuric acid and the ethereal solution extracted with alkali and acidified with hydrochloric acid when α -naphthoic acid was precipitated in almost quantitative yield. It was recrystallised from 25% alcohol. (Ber., 1904, 37, 625).

Molecular proportions of the acid and phosphorous/

phosphorous-pentachloride were mixed together and warmed on a steam bath until reaction was completed; the phosphorous-oxychloride distilled away and the residual α -naphthoylchloride distilled in vacuo. It had b.p. $173^{\circ}/15\text{mm}$. (Ber., 1905, 38, 180).

The same acidchloride was also obtained in a similar way by using thionylchloride instead of phosphorous pentachloride.

Catalytic reduction to α -naphthaldehyde.



This reaction was carried out at a temperature of 160° with a quantity of 5gms of acidchloride at a time, dissolved in 25 c.c. xylene in which 2 gms of catalyst were suspended.

The palladium-bariumsulphate catalyst was prepared as follows.

Twelve gms. of freshly precipitated barium-sulphate were made into a paste with 235 c.c. of hot water and 1 gm of palladium chloride in a solution of 40 c.c. of water added. After addition of 1 gm. of formalin the solution was made alkaline with sodium hydroxide and the whole heated to boiling for some time. The precipitate readily settled out and was filtered off and dried carefully in vacuo, being now/

now ready for the reduction.

Hydrogen from a Kipp was passed through a series of washbottles, containing a, potassium permanganate and b, conc. sulphuric acid and then finally dried by passing it over phosphorous pentoxide. It was led in a very slow stream into the boiling xylene solution. Hydrochloric acid was slowly evolved and ceased after about 4 or 5 hours. The solution was then filtered from the catalyst and the aldehyde extracted in the usual way with sodium bisulphite. From this addition compound, the aldehyde was liberated with warm sodium carbonate solution and extracted with ether.

The resulting oil distilled at $152^{\circ} / 13 \text{ mm.}$ and was obtained in an average yield of 60%. It gave a phenylhydrazone (m.p. 234° , red needles) and a semioxamzone (m.p. 258°).

This showed that the catalytic reduction method could be employed for the naphthalene series and the preparation of 3 and 5-methoxy- α -naphthaldehydes, described later, was carried out in a similar manner.

A Cannizzarro reaction was then tried on this aldehyde in order to see if the naphthaldehydes can be converted in this way to the corresponding carbinols.

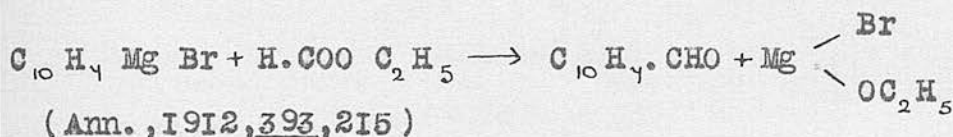
α -Naphthaldehyde gave fairly readily α -naphthylcarbinol (m.p. 59° - 60°) with 25% alcoholic potassium hydroxide/

hydroxide.

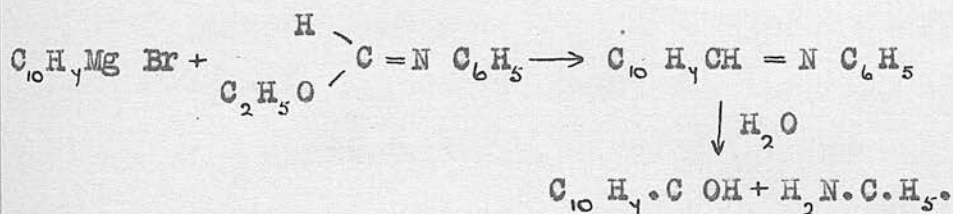
Experiments were now carried out to see whether brominated methoxy naphthalenes can be used for the preparation of

- a. methoxy - naphthaldehydes and
- b. methoxy - naphthylcarbinols.

Methods attempted for aldehyde synthesis were:



and



This expectation was not realised because of the difficulties experienced in the preparation of 1-methoxy-5-bromonaphthalene, which could not be obtained in quantities suitable for use as starting materials.

In the case of the 2-methoxy-1-bromonaphthalene, the compound refused to react with magnesium and hence 2-methoxy-1-naphthyl-carbinol could not be prepared thus.

This is probably due to steric hindrance, since a certain amount of reaction is effected by the/

the methoxy-group in ortho position to the bromine ~~at~~ atom.

The other experiments by which it was hoped to go directly from halogenated naphthalene to naphthylcarbinols gave α -naphthylcarbinol (Ber.,¹ 1921, 54, 739; 1922, 55, 3406) but no substituted carbinol was prepared thus, because of the difficulty of obtaining 1:4 and 1:5-methoxy-bromonaphthalene, whilst 2:1-methoxy-bromonaphthalene refused to react with magnesium as already stated.

α -Naphthylcarbinol.

Magnesium (8 gms.), 30 c.c. ether and 3 gms. ethyliodide were allowed to react together and then 64 gms. of α -bromonaphthalene, dissolved in 150 c.c. ether added to the mixture. When the vigorous reaction had ceased, formaldehyde vapour, produced by heating 25 gms. of trioxymethylene in a retort, was passed in. The whole was continuously stirred and the temperature ^{kept} at 5°.

After working up the reaction mixture in the usual manner, a small yield of α -naphthylcarbinol was obtained as white needles of m.p. 59.5 - 60° and b.p. 301° / 760 mm.

A large number of experiments were carried out in the hope of improving the yields of carbinol. It would have been a very valuable method, but the quantity of carbinol obtained did not justify the adoption of this method for other cases.

2-Methoxy- α -naphthaldehyde and

4-methoxy- α -naphthaldehyde. (Ann. 1907, 357, 365.)

α and β Naphthyl methyl ethers were obtained as follows:

The naphthol (50 gms.), methyl alcohol (50 gms.) and conc. sulphuric acid (10 gms.) were heated together at 125° for 4 hours under a reflux condenser and slight pressure, produced by a mercury valve.

The solution was then poured into cold water and the oil which separated washed with sodium hydroxide and distilled. Any unchanged naphthol was recovered from the solution.

α -naphthylmethyl ether has b.p. 269° and

β -naphthylmethyl ether b.p. 274° and

m.p. 72°

To 50 gms. of α -naphthylmethyl ether dissolved in 200 gms. of dry benzene 70 c.c. hydrocyanic acid, and 70 gms. of powdered aluminium chloride were added. The whole was immersed in a freezing mixture and a current of dry hydrogen chloride passed into the solution for about 2 hours, the temperature being allowed to rise slowly from 0° to 45°.

By pouring the reaction mixture on^{to} ice, the aldimine hydrochloride was decomposed and after acidification of the whole with hydrochloric acid, benzene and any unchanged naphthylether were removed by steam distillation and the residue extracted with ether/

ether.

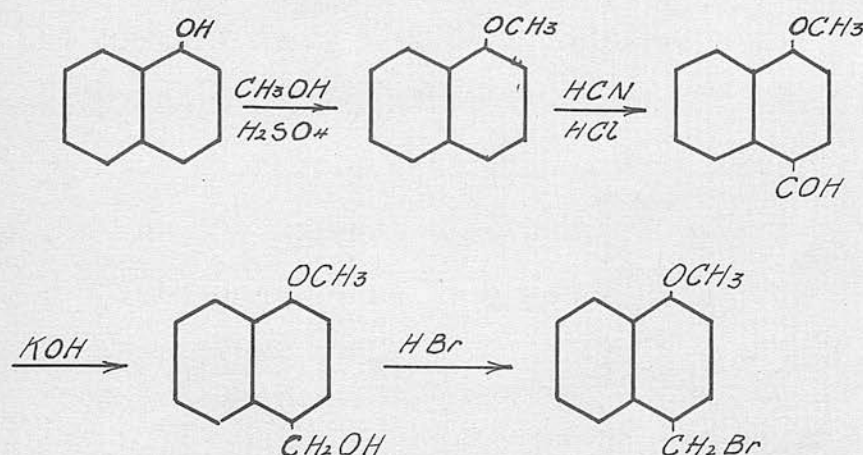
Both aldehydes were purified by conversion into bisulphite compounds.

The 2-I-aldehyde had m.p. 84° and the 4-I distilled at $200^{\circ}/16\text{mm}$.

Average yield obtained was 60%.

4-Methoxy- α -naphthyl-methyl-bromide.

This was obtained according to the following scheme:



(The corresponding 2-methoxy- α -naphthyl methyl bromide could not be obtained for reasons given later.)

Many attempts were made to convert these aldehydes into the methoxy-naphthyl-methylcarbinols, but only in the case of the 4-I compound were they successful.

In both cases, alcoholic potassium-hydroxide of various concentration and of different temperature were used. Even when these methoxy-aldehydes were submitted/

submitted to exactly the same treatment which worked successfully with the unsubstituted α -naphthaldehyde which yielded α -naphthylcarbinol (see page 23.) no change was observed. Example, when 25 gms. aldehyde was allowed to stand in contact with 75 c.c. of 25% potassium hydroxide (19 gms. KOH in 14 c.c. H₂O made up 75 c.c. with alcohol) for 25 hours or longer at room temperature no reaction took place.

Finally a large excess of a concentrated aqueous solution of potassium hydroxide (30 gms. of aldehyde and 20 gms. of KOH in 15 c.c. H₂O standing for twenty-four hours) gave the desired 4-methoxy-4-naphthyl carbinol. After diluting with water the carbinol was extracted with ether, dried over sodium sulphate and the solvent then evaporated off.

It crystallised from petrol ether in light, colourless needles of m.p. 35°. (Chem. Abstracts, 1920, 14, 3406).

4-Methoxy- α -naphthyl-methyl bromide was prepared by passing hydrobromic acid into a warm benzene solution of the carbinol. A yellow solid precipitated immediately which, when saturation with hydrobromic acid was completed, was filtered off and quickly transferred to a desiccator.

Description of the yellow crystals obtained.

The solid fumed in air and could not be recrystallised because of its marked instability.

Under/

Under the microscope long prismatic needles could be discerned, which however slowly disappeared. In cold water it rapidly became liquid, due to hydrolysis and bromidion could be detected with silver nitrate. It was impure 4-methoxy- α -naphthyl methyl bromide, m.p. about 110° .

It was immediately hydrolysed by aqueous alcohol as described in the experimental part.

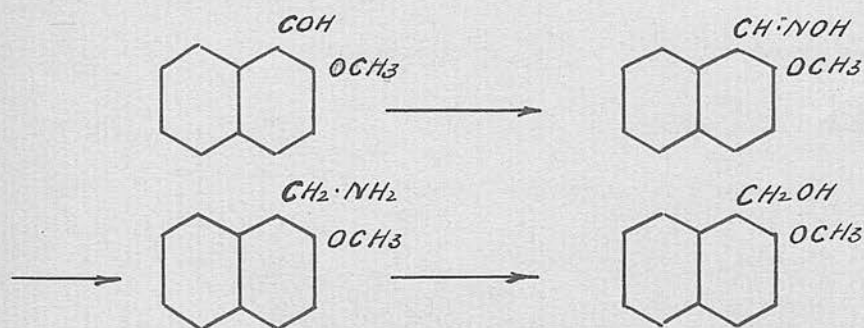
Investigation of the action of potassium hydroxide on 2-methoxy- α -naphthaldehyde showed that this reagent even as very concentrated solution at a temperature/

temperature over 100° does not reduce the aldehyde to the corresponding carbinol.

The ortho position of the methoxy group is probably the cause of this steric influence of the aldehyde group.

A similar fact was observed by Gattermann (Ann., 1888, 244, 72) who discovered that whilst 4-methoxy- α -naphthoamide is hydrolysable with potassium hydroxide the corresponding 2- derivative is unreactive to this reagent.

Two methods of converting aldehydes into carbinols directly were tried. The first is summarised as follows:



2-Methoxy- α -naphthaldoxime was not reduced by sodium-amalgam in glacial acetic acid, a reaction which goes readily in the benzene series.

The second method consisted of an attempt to reduce ^{hydroxy}aldehyde to alcohol by means of aluminium amalgam.

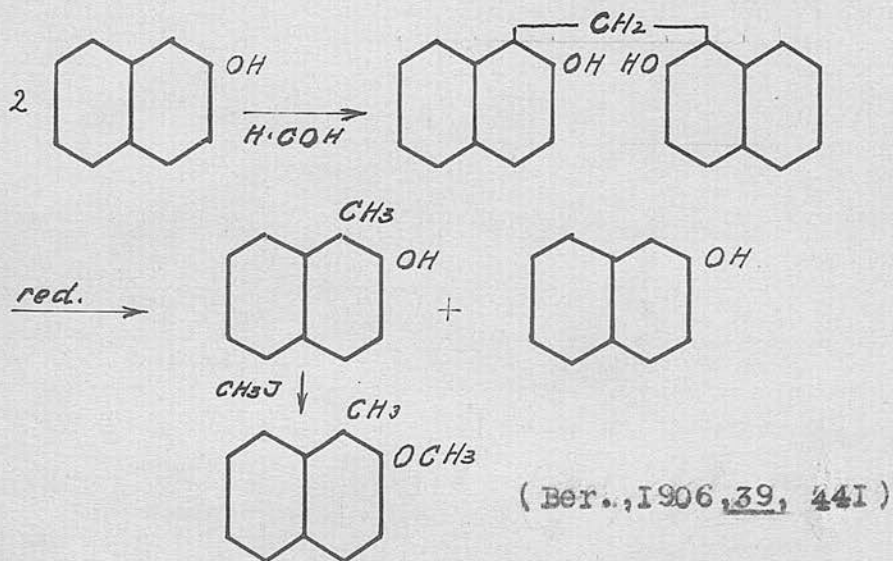
Ten grams of 2-hydroxy- α -naphthaldehyde dissolved in 250 c.c. ether were left in contact with activated aluminium foil, for 24 hours. The solvent was filtered/

filtered and the residual solid treated with 6% hydrochloric acid and after drying shaken with cold chloroform. The remaining undissolved substance was filtered again and dissolved finally in hot chloroform, from which ~~whereof~~ 2-hydroxy- α -naphthyl-carbinol crystallised out in long white needles of m.p. 189°.

This reduction could not be carried out on a large scale.

The small yields of only 5% are due to formation of intermediate compounds as described by Betti and Mundici (Gazzetta chim.ital. 1906, 36, 659).

An attempt was made to obtain 2-methoxy- α -naphthyl-methyl bromide by bromination of I-methyl- β -naphthyl methylether, prepared as follows:



Preparation of dinaphthyl methane

To β -naphthol (100 gms.) dissolved in 120 c.c. alcohol/

alcohol, 55 c.c. of 40% formaldehyde and 20 gms. of crystalline sodium acetate were added, and the whole allowed to stand for four days at room temperature. The crystalline precipitate was then filtered off and recrystallised from glacial acetic acid, it had m.p. 200°.

I-methyl-2-naphthol.

Dinaphthylmethane (60 gms.) dissolved in sodium hydroxide solution (60 gms. NaOH in 600 c.c. of water) was reduced with zinc dust (75 gms.) by boiling the whole for 8 hours under reflux condenser. I-Methyl-2-naphthol and β -naphthol were formed of which the latter was converted back to dinaphthylmethane by a further addition of formaldehyde after which the whole was again submitted to the action of zinc dust.

Those proceedings were repeated until almost all the β -naphthol had been converted to I-methyl-2-naphthol.

The solution was now filtered from the zinc dust and formaldehyde again added, in order to react with the residual β -naphthol, which thus could be separated. On acidification of the filtrate a mixture of I-methyl-2-naphthol and dinaphthylmethane was precipitated and separated from each other by boiling with much water, in which only methyl-naphthol is soluble. I-methyl-2-naphthol had m.p. 110°.

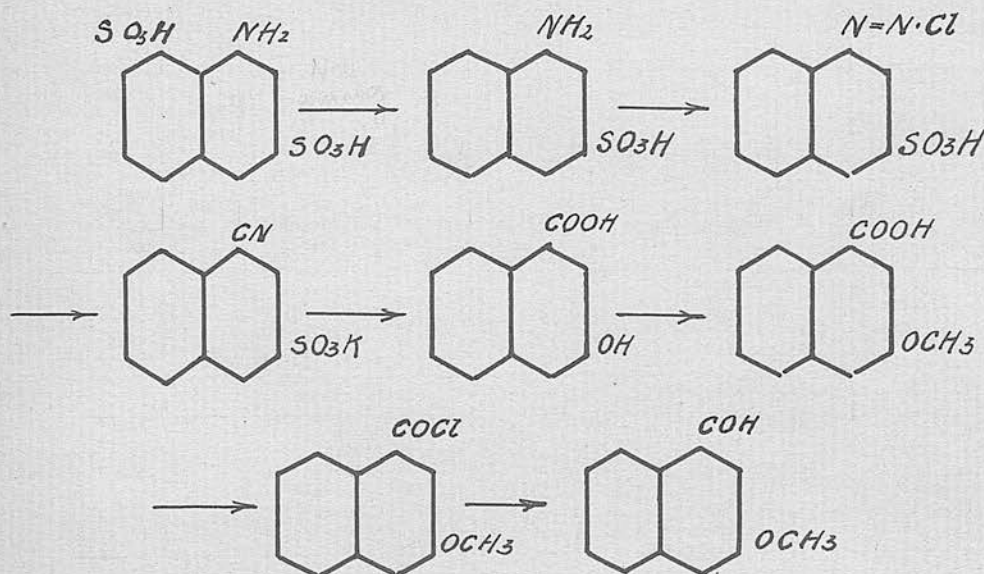
The methylether was prepared from the potassium salt of I-methyl-2-naphthol with methyl iodide in alcoholic/

alcoholic solution and after recrystallisation from methyl-alcohol 1-methyl-2-methoxy naphthalene was obtained, with m.p. 39°.

The bromination of this compound yielded only a tarry mass from which no crystalline substance could be obtained.

Attempts to obtain 3-Methoxy- α -naphthyl methyl bromide
3-Methoxy- α -naphthaldehyde.

This compound was synthesised according the following scheme



In order to prepare 3-methoxy- α -naphthoic acid the method of Royle and Schedler (J.C.S., 1923, 143, 164D) was modified in two important places.

The 1-naphthylamine-3-8-sulphonic acid was supplied in moderately pure condition by the British Dyestuffs Corporation and instead of removing the sulphonic/

sulphonic group in the 8 position by boiling the acid with 75% sulphuric acid, (the method employed by Royle and Schedler) the amino-sulphonic acid was reduced by sodium amalgam as follows. One Hundred grams of the acid were dissolved in 1000 c.c. of water and 25 gms. of sodium hydroxide, and vigorously agitated at ordinary temperature whilst 200 gms. of 4% sodium amalgam were slowly added during 2 hours. The mercury was then separated, the solution filtered and then acidified with conc. hydrochloric acid. The α -naphthylamine-3-sulphonic acid was precipitated pure and quantitative ^{yields} were obtained. No crystallisation was necessary. (Sulphur content was 14.0% as against 14.3% calculated.)

Seventy-five per cent. boiling sulphuric acid caused the 3-8-acid to char badly, probably owing to commercial impurities.

Diazotation of α -naphthylamine-3-sulphonic acid.

Forty six grams ($2/10$ of a mol) of the acid dissolved in aqueous solution of 9 gms of sodium bicarbonate in 120 c.c. water was cooled to about 0° and 130 c.c. of conc. hydrochloric acid added. The finely divided suspension was diazotised by the gradual addition of 14 gms of sodium nitrite in 40 c.c. of water, the temperature now being maintained below 5° , After the solution had been saturated with sodium-chloride the crystalline 1-3-Diazonium chloride of canary-yellow colour/

colour was filtered and washed, and to it a hot solution (60°) of cuprous cyanide ^{in potassium cyanide} added. (The cuprous cyanide was made up from 62 gms. copper sulphate in 250 c.c. water and 55 gms. sodium cyanide in 100 c.c. water, for every 46 gms of α -naphthylamine-3-sulphonic acid used.)

Nitrogen was immediately evolved and the reaction was completed by warming the whole for one hour on a steam bath. Concentrated hydrochloric acid was then added to the hot solution, the precipitated cuprous cyanide filtered off and washed with a little hot water, the washings and filtrates were then evaporated to dryness on the steam bath in a round bottomed flask, fitted with a steam trap, under reduced pressure.

Care must be taken, that any excess of hydrochloric acid is carefully avoided since otherwise a troublesome tar is formed. The residues were extracted several times with 90% alcohol in the same flask and then most of the alcohol distilled off under reduced pressure, when the nitrile crystallised out in fairly pure condition, ready to be converted, into the potassium salt.

It was readily formed on warming the nitrile with the calculated quantity of potassium carbonate in aqueous solution. The potassium salt crystallised in long red needles when the solution was cooled and
if/

if necessary saturated with potassium chloride. It may be recrystallised from potassium chloride solution.

The preparation of the potassium salt is accompanied by a slight hydrolysis of the acid to the α -naphthoic-3-sulphonic acid, ammonia being evolved, a reaction which does not influence the obtaining of the hydroxy-naphthoic acid. Royle and Schedler converted this nitrile first to the carboxy-naphthalene-sulphonate and fused it with caustic soda.

They boiled the potassium salt of the cyan-sulphonic acid with 10% potassium hydroxide until ammonia ceased to evolve and removed final traces of copper by means of hydrogen sulphide, passed into the boiling acidified solution which was then filtered and evaporated until crystals began to appear. On standing almost the whole of the desired potassium carboxy-naphthalene-sulphonate crystallised out.

It was found however that the separation of the intermediate compound is not necessary at all, but the conversion of the CN group into the COOH can readily be combined with that of the SO_3H group to the hydroxyl (compare D.R.P. No. 413836).

The finely powdered anhydrous sulphonate was added gradually to fused sodium hydroxide at 180° . Each charge of 25 gms. required 250 gms. of sodium hydroxide and 50 c.c. water. The mass became dark red and was vigorously stirred. Ammonia was evolved in quantity. After having been heated to 230 the melt solidified/

solidified gradually. This took place usually after $\frac{5}{4}$ of an hour. After dissolving the resulting solid in water, the solution was almost neutralized with conc. hydrochloric acid, animal charcoal added to the hot solution and the whole left standing for about 2 hours. From the filtered slightly brown coloured solution the 3-hydroxy- α -naphthoic acid was precipitated with conc. hydrochloric acid. The acid, recrystallised from boiling water or dilute alcohol had m.p. 242° and average yield obtained, calculated from the starting material used, namely 1-naphthylamine-3-8-disulphonic acid was 18%.

Methylation of 3-methoxy- α -naphthoic acid.

The acid dissolved in an excess of 5% sodium hydroxide solution was shaken or stirred with an excess of dimethyl-sulphate, care being taken to prevent the mixture from becoming acid. The reaction was carried out at $40-60^{\circ}$, but was discovered to be incomplete, although many variations were tried. The solution was filtered whilst still alkaline to remove a small quantity of tar and then acidified with hydrochloric acid. The precipitated methoxy acid was filtered off and twice recrystallised from alcohol. It had m.p. 154° instead of 159° .

So far, the experimental work was carried out, except for two variations, according to the methods of Royle and Schedler. The subsequent results were /

were obtained after many attempts to overcome the extraordinary difficulties experienced in this branch of naphthalene chemistry.

The methylation was continued as follows. The methoxy acid remaining in solution after crystallising the main quantity was once more methylated and in order to separate hydroxy and methoxy compound it was hoped that fractionate crystallisation could be used.

It was found however, that the 3-methoxy- α -naphthoic acid which had m.p. 159°, still contained traces of unmethylated hydroxy naphthoic acid, the presence of which was fatal for the preparation of the corresponding acid chloride and aldehyde. To free the methoxy acid from the hydroxy acid, advantage was taken of the fact that the latter forms an insoluble red dye with diazotised sulphanilic acid whilst the former remains unchanged.

The impure methoxy-naphthoic acid was dissolved in dilute sodium hydroxide and diazotised sulphanilic acid solution was added until no more red colour was formed. After standing for 25 hours, the acid was precipitate with hydrochloric acid, filtered and carefully dried. The whole was then extracted with benzene in a Soxhlet apparatus when pure methoxy-naphthoic acid of m.p. 160° was obtained, the insoluble red dye remaining in the extraction thimble.

After this treatment, the yields diminished considerably/

considerably. The methoxy-naphthoic acid was converted to the corresponding acid chloride as follows.

Ten grams of the purified potassium salt, obtained by the addition of a theoretical quantity of 20% alcoholic potassium hydroxide and subsequent evaporation to dryness, were added to a vigorously stirred mixture of 18 gms. of benzene and 18 gms. of thionylchloride at ordinary temperature. The reaction mixture was then warmed on a steam bath and potassium chloride settled out, when it was filtered hot and washed with anhydrous ether. The remaining benzene, ether and excess of thionylchloride were evaporated in vacuo and the residual liquid distilled under diminished pressure, a process, which is impossible if any traces of hydroxy acid are present. The chloride may also be crystallised from petroleum ether (b.p. 40° - 60°) from which it crystallises in yellow needles of m.p. 79° , (Found Cl: 15.25; $C_{12}H_9O_2Cl$ requires Cl 16.08%) but even then, if hydroxy acid is present, the chloride is useless for catalytic reduction.

3-Methoxy- α -naphthaldehyde was obtained in the same apparatus as that in the preliminary experiments, which showed, that Rosenmunds catalytic reduction could be extended to naphthoylchlorides in order to obtain naphthaldehydes.

The quantities used were

0.6 gms. of 3-methoxy- α -naphthoyl chloride,
1 gm. of catalyst and 10 c.c. of xylene at a
temperature/

temperature of 160°.

The reduction was completed in four hours, when the hot xylene solution was filtered from the catalyst and ~~then~~ shaken with sodium bisulphite solution for several hours, when a white addition compound was formed. This was decomposed with warm sodium carbonate solution and the aldehyde extracted with ether. It crystallised from petroleum ether in beautiful rhombic plates, which have m.p. 60°. Found: C, 77.12; H, 5.35, $C_{12}H_{10}O_2$ requires C, 77.45; H, 5.37.%

It gave p-nitrophenyl hydrazone, brick red needles m.p. 197°, semicarbazone, white needles from aqueous alcohol m.p. 200° and oxime, white needles from aqueous alcohol, m.p. 102°.

3-Methoxy- α -naphthyl carbinol.

This compound was obtained from the aldehyde (0.9gms.) which was allowed to stand for 3 days in contact with 1 c.c. of 66% potassium hydroxide, being heated on the water bath every 24 hours for 10 minutes. 3-methoxy- α -naphthyl carbinol crystallises from

water in fine, colourless needles which have m.p. 88°.

Found: C: 76.1%; H: 6.42%; $C_{12}H_{12}O_2$ requires

C: 76.50%; H: 6.38%.

The quantity of 3-methoxy- α -naphthyl carbinol (5 mg.) finally obtained was so small that it was not possible to proceed to the 3-methoxy- α -naphthyl methyl bromide. In the course of this synthesis, yields/

yields were found to be very poor, especially on account of the necessity for great purity in the reduction of the acid chloride.

These investigations however opened up a way which lead to the preparation of various isomeric methoxy-naphthyl carbinols, of which the 1:5 (and ^{The 1:5} 1:3 as above) were prepared, ~~and~~ will be described in the following section.

In order to see if the hydroxy-naphthoic acids could be readily obtained, the distillation of a mixture of sodium- α -naphthylamine- β -sulphonate with twice its weight of finely powdered potassium ferrocyanide was attempted. Appreciable quantities of ammonia were evolved. From the dark oil which distilled over only a small quantity of pure naphthonitrile was obtained which was hydrolysed by boiling with sulphuric acid and yielded after crystallisation 4-amino- β -naphthoic acid which had m.p. 205° .

Since it was not found possible to increase the yields of amino-naphthoic acid, the conversion to hydroxy-naphthoic acid by means of diazotation and hydrolysis was not attempted and the scheme was abandoned in favour of the synthesis which has been described in the previous pages.

Preparation/

Preparation of5-Methoxy- α -naphthyl methyl bromide.5-Methoxy- α -naphthaldehyde.

5-Methoxy- α -naphthaldehyde has been prepared by the catalytic reduction of 5-methoxy- α -naphthoyl-chloride in a similar manner to the one described for the 3-methoxy- α -naphthaldehyde.

α -Naphthylamine-5-sulphonic acid was converted into 1-cyanonaphthalene-5-sulphonic acid by the ~~met~~ method of Royle and Schedler (J.C.S., 1923, 123, 1643) and then by the addition of the calculated quantity of potassium carbonate into the corresponding potassium salt, 25 gms. of which (in small quantities at a time) were added to a vigorously stirred, fused mixture of 250 gms. of sodium hydroxide and 50 gms. of water at a temperature which was allowed to rise slowly from 180° to 230°. (compare O.R.R 413836). The mass, which finally became a solid, was cooled and 5-hydroxy- α -naphthoic acid was liberated from its aqueous solution by addition of conc. hydrochloric acid; after recrystallisation from dilute alcohol the acid melted at 235°.

The acid (20 gms.) dissolved in a solution of 15 gms. of potassium hydroxide in 280 c.c. of water, was vigorously stirred with 15 gms. of dimethyl sulphate at 50° for about 1 hour, and the alkaline solution filtered and acidified. The 5 methoxy- α naphthoic/

naphthoic acid so precipitated was obtained free from the corresponding hydroxy-acid by allowing it to stand in an alkaline solution of diazotised sulphanilic acid for 24 hours, after which the solution was acidified and the precipitate carefully dried and extracted with benzene.

Any sample of the corresponding acid chloride obtained from 5-methoxy- α -naphthoic acid which was not treated in such a way was very difficult to distil. A tarry residue was left in the distillation flask, containing almost all acid chloride which was put into it.

As in the 3-methoxy- α -naphthoic acid the 5-methoxy- α -naphthoic acid m.p. 228° (compare Fuson, J. Amer. Chem. Soc., 1924, 46, 2787) had to be quite free from the hydroxy-acid before conversion into the acid chloride.

The acid was dissolved in the calculated quantity of 20% alcoholic potassium hydroxide, and the solution evaporated to dryness. The dried potassium salt (10 gms.) was added to a large excess of vigorously stirred thionyl chloride (18 c.c.) in the same quantity of dry benzene. The whole was finally heated on the water bath for about 5 minutes, cooled and filtered from precipitated potassium chloride and acid, and then the benzene and thionyl chloride were evaporated ^{off} / under reduced pressure. The residual 5-methoxy- α -naphthoyl chloride was distilled in vacuo.
It/

It had b.p. 194° /II mm. and m.p. $80-81^{\circ}$ in heavy canary yellow coloured needles from petrol ether.

Analyses:

Found: Cl 15.7%; $C_{12}H_9O_2Cl$ requires Cl 16.0%.

5-Methoxy- α -naphthaldehyde.

5-methoxy- α -naphthoyl chloride (5 gms.) in xylene (25 c.c.) in contact with palladinised barium sulphate was reduced by a current of dry hydrogen for five hours, the temperature of the bath being 170° . (compare Rosenmund, Ber., 1918, 51, 591). The aldehyde was separated in the usual manner as the bisulphite compound. It crystallised from light petroleum ether in light yellow plates, m.p. 66° .

Analyses:

Found: C, 77.45 ; H 5.5

$C_{12}H_{10}O_2$ requires C, 77.45 ; H 5.4%.

The p-nitro phenylhydrazone forms red needles m.p. 246° from dilute acetic acid, the semicarbazone, fine needles m.p. 246° , from dilute acetic acid and the oxime, needles m.p. 104° , from water or aqueous alcohol.

α -Naphthol, β -naphthol and their methyl ethers were submitted to the action of hydrogen in a similar manner, in order to confirm that a ring reduction does not take place. No change was observed.

In order to ascertain the rate of reduction of the acid chloride, the amount of hydrogen chloride evolved was titrated with standard alkali solution as shown/

shown in the following table and in Fig.I page 47.

Hours	% acid chloride reduced
$\frac{1}{2}$	40
1	60
$1\frac{1}{2}$	71
2	78
3	86
4	91
5	93
6	94

In order to obtain

5-Methoxy- α -naphthyl carbinol, the aldehyde was submitted to the action of aqueous potassium hydroxide as follows.

5-Methoxy- α -naphthaldehyde (5 gms.) was allowed to stand for 3 days in contact with 66% potassium hydroxide (5 gms. KOH -3 c.c. water and 1 c.c. absolute alcohol.) Every 24 hours the whole was heated on a steam bath for 10 minutes to a temperature of 70° and was allowed to cool slowly to room temperature.

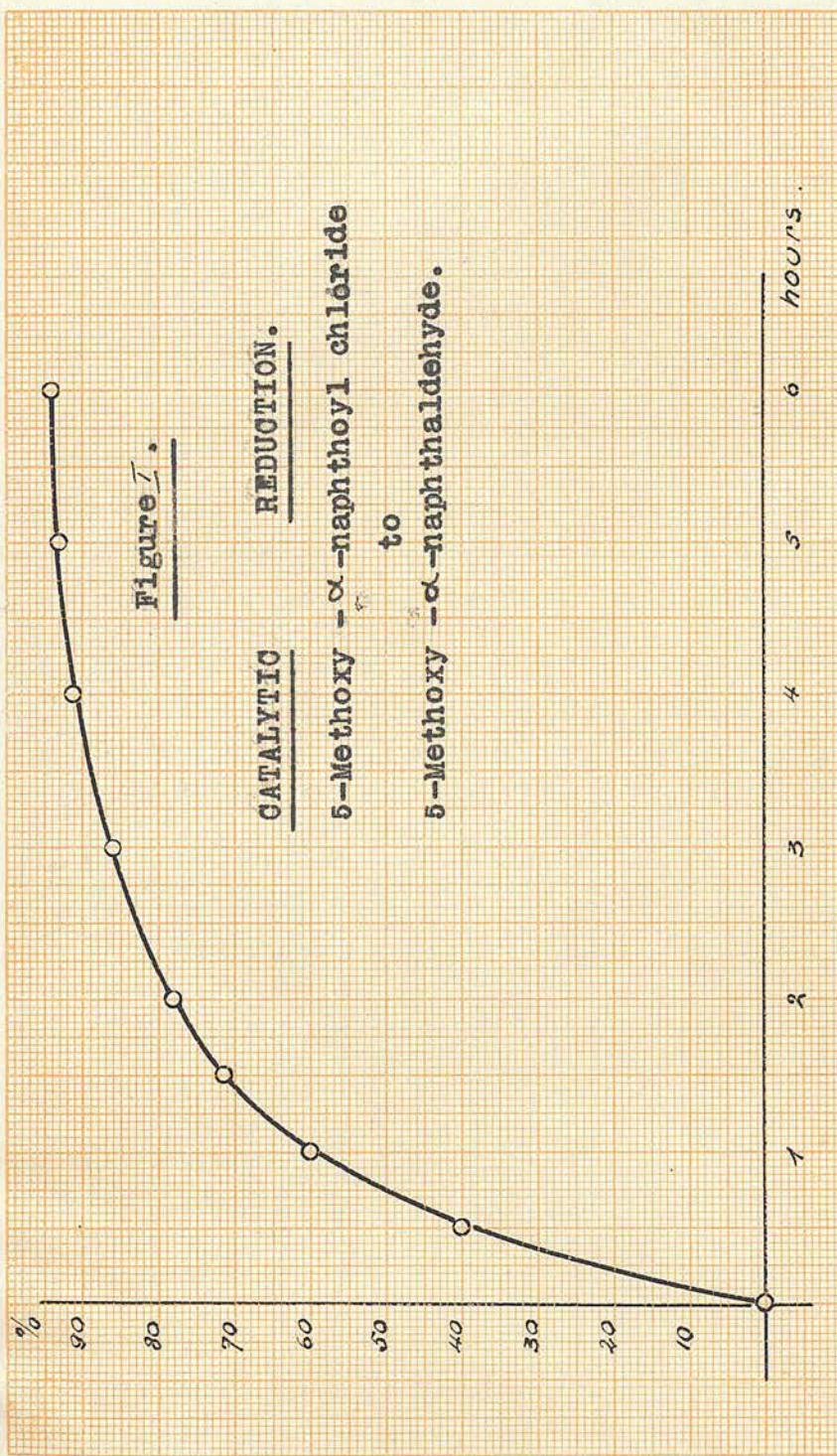
5-Methoxy- α -naphthyl carbinol crystallised from water in colourless needles and had m.p. 98°. (Found: C, 76.5%; H, 6.34%; $C_{12}H_{12}O_2$ requires C, 76.5%; H, 6.38%).

5-Methoxy- α -naphthyl methyl bromide,

was prepared by passing dry hydrogen bromide into a warm benzene solution of the carbinol, until saturation was completed. The liquid was then separated from the water, which was formed during the bromination/

bromination and evaporated to dryness in a desiccator. The solid residue was then extracted with petroleum ether (b.p. 40 - 60°). It crystallised from this solvent in white prismatic needles of m.p. 65-66°. Found Br, 31.2% $C_{12}H_{11}O$ Br requires Br 31.9%. The compound is not lacrimatory but produces a burning sensation on the skin and does not fume in the air as the 1:4 compound does.

The hydrolysis of 5-methoxy- α -naphthyl methyl bromide is described in the experimental part.



Preparation of 1:6 and 1:7 methoxy- α -naphthoic acid.

These experiments were undertaken in the hope of obtaining 6-methoxy- α -naphthyl methyl bromide, in a manner similar to that described for 5-methoxy- α -naphthyl methyl bromide.

The necessary α -naphthylamine-6-sulphonic acid was supplied by British Drug Houses Ltd., After 900 gms. of this starting material had been converted to the naphthoic acid, via the nitrile, it was discovered that it was not pure 1:6 compound but contained at least 60% 1:7 isomeride. As a mixture of these two hydroxy-naphthoic acids would not have served the purpose to obtain pure end products, various attempts were made to separate these compounds. Owing to the fact that both isomerides did not vary sufficiently in solubility in any solvents to ensure a successful separation by means of fractionate crystallisation, the solubility of barium, calcium and sodium salts was investigated. Contrary to expectations, it was found that the barium and calcium salts of both acids were very soluble in water and only the difference of solubility of the sodium salts led to the hope of a successful separation. After the mixture had been roughly divided into two parts, one of which was chiefly 1:6 with a little 1:7 and the other 1:7 with a little 1:6 hydroxy-naphthoic acid, by fractional crystallisation/

crystallisation from dilute alcohol, in which the 1:6 isomeride is the more soluble, the two parts were purified separately as follows. The hydroxy naphthoic acids were dissolved in a small bulk of hot sodium carbonate solution. When this was allowed to cool slowly, the sodium salt of 7-hydroxy- α -naphthoic acid crystallised out and was digested with a small quantity of water in order to dissolve the traces of the more soluble salt of the 1:6 isomeride which might have crystallised out too. This process was repeated several times and thus rendered possible the obtaining of a very pure 7-hydroxy- α -naphthoic acid of m.p. 255°.

It was still more difficult to obtain pure samples of 6-hydroxy- α -naphthoic acid of m.p. 209° which could be however separated in a pure condition by sufficient repetitions of the fractional crystallisation.

It could not have been foreseen that a product supplied as α -naphthyl amine 6-sulphonic acid would contain more than 50% of its 1:7 isomeride, otherwise the trouble ~~of~~ some process of separation could have been avoided and the purification carried out at the naphthyl-amine sulphonic acid stage by means of their sodium salts.

6-Methoxy- α -naphthoic acid and

7-Methoxy- α -naphthoic acid.

These compounds were obtained by methylating
the/

the corresponding hydroxy-naphthoic acids with excess of dimethyl sulphate.

6-Methoxy- α -naphthoic acid crystallised from aqueous alcohol or petroleum ether in colourless prismatic needles of m.p. 183° .

Found C, 69.20; H, 5.1; $C_{12}H_{10}O_3$ requires C

C, 69.23; H, 4.81.

7-Methoxy- α -naphthoic acid crystallised from petroleum ether in colourless silky needles of m.p. 169° .

Found C, 69.50; H, 5.10; $C_{12}H_{10}O_3$

requires C, 69.23 H, 4.4;

Neither acid would give a crystalline potassium salt and the action of thionyl chloride and even of phosphorous penta chloride gave very impure acid chloride from which only a trace of aldehyde could be obtained.

1-Bromo- β -naphthyl-methyl bromide and

4-Bromo- α -naphthyl-methyl bromide.

These compounds were obtained according to the method of Mayer and Sieglitz (Ber., 1922, 55, 1839) by bromination of α and β -methylnaphthalene and side chain bromination of the reaction products.

To α and β -methylnaphthalene (47.4 gms.) dissolved in carbon disulphide, 54 gms. of bromine were slowly added, and the whole warmed on a steam bath until the solutions became bright yellow. After evaporation away of the hydrobromic acid and carbon disulphide the compounds were distilled under reduced pressure.

1-Bromo- β -methyl naphthalene had b.p. 165-170° / 13 mm. and 4-Bromo- α -methyl naphthalene 162-164° / 12 mm.

The side chain bromination of both compounds was carried out at 210°, at which temperature bromine (32 gms.) was added to the bromo-methylnaphthalene (44 gms.), within 20 minutes, a current of air being passed all the time to ensure efficient bromination.

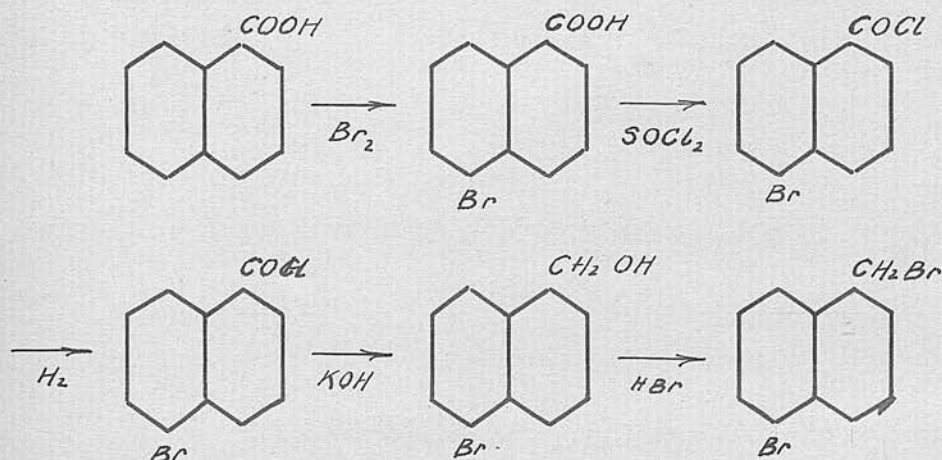
The reaction products were then cooled and the solids recrystallised from ligroin.

4-Bromo- α -naphthyl methyl bromide crystallised in white needles of m.p. 104° and 1-Bromo- β -naphthyl methyl bromide in similar needles of m.p. 107-108°.



5-Bromo- α -naphthyl methyl bromide.

This compound was obtained by the following series of reactions:



5-Bromo- α -naphthoic acid was prepared by the method of Hausmann (Ber., 1876, 9, 1517; J. f. pr. Chemie 1888, 38, 155; J. Amer. Chem. Soc., 1925, 47, III9).

α -Naphthoic acid, dissolved in glacial acetic acid was warmed and an excess of bromine added. On cooling, the brominated naphthoic acid crystallised out, was filtered off, washed with acetic acid and crystallised from alcohol. It had m.p. 261°.

Previous investigators have given the melting point of the acid as 242° and 246°, but it was found to be 261°, after several crystallisations from 90% alcohol from which it was obtained as large, white plates. (Found: Br, 31.40%; $C_{10}H_7O_2Br$ requires Br 31.85%.)

5-Bromo- α -naphthoyl chloride, (J. Amer. Chem. Soc., 1925, 47, III9) was prepared as follows. 5-bromo- α -naphthoic acid/

acid (20 gms.) mixed with 5 molecular proportions of thionyl chloride were heated under reflux condenser on a steam bath, until solution of the acid was completed. (Five hours were necessary). The liquid was then cooled and filtered and unchanged thionyl chloride distilled off under reduced pressure. The residue, which solidified on cooling gave a 70% yield of the chloride in colourless plates, which, when crystallised from petroleum ether (b.p. 80-100°) had m.p. 84°.

This acid chloride was then submitted to catalytic reduction with hydrogen in presence of palladised barium sulphate under similar conditions to those adopted for methoxy-naphthoyl chlorides. The aldehyde was again extracted with sodium bisulphite and the addition compound decomposed with concentrated sodium carbonate solution.

5-Bromo- α -naphthaldehyde has m.p. 103-107°, and crystallises from petroleum ether (b.p. 80-100°) in colourless prismatic needles.

(Found: Br 33.85%; C₁₁H₉OBr requires 34.05%),
p-nitro-phenyl hydrazone m.p. 263° from acetic acid;
semicarbazone, colourless needles from aqueous acetic acid m.p. 263°; and oxime, colourless needles from aqueous alcohol, m.p. 138-139°.

5-Bromo- α -naphthyl carbinol

was obtained from the aldehyde (1.5 gms.) which was allowed/

allowed to stand for three days in contact with 66% aqueous potassium hydroxide, being heated on the steam bath every 24 hours for 10 minutes. 5-Bromo-naphthyl carbinol crystallised from petroleum ether (b.p. 80 - 100°) in fine white needles of m.p. 124°. (Found C, 56.0 H, 4.1 ; $C_{11}H_9OBr$ requires C, 55.69; H, 3.81.%

5-Bromo- α -naphthyl methyl bromide.

was prepared by passing dry hydrogen bromide into a warm benzene solution of the carbinol, until saturation was completed. The liquid was then separated from the water which was formed during bromination and evaporated to dryness in a desiccator. The solid residue was then extracted with petroleum ether (b.p. 40° - 60°). It crystallised from this solvent in white needles of m.p. 101°.

(Hydrolysable bromine 26.7%, $Br \cdot C_{10}H_6 \cdot CH_2Br$ requires 26.8%).

The compound is not lacrimatory but produces a burning sensation on the skin.

The hydrolysis of 5-bromo- α -naphthyl methyl bromine is described in the experimental part.

EXPERIMENTAL.Reduction of mono-halogenated naphthalene derivatives and α - and β -naphthol by means of hydrø iodic acid.

α - and β -bromo, α - and β -iodo naphthalene and α - and β -naphthol were reduced in a thermostat at 100°.

Approximately 0.17 gm. of these compounds were weighed out in 25 c.c. standard flasks. Ten c.c. of glacial acetic acid and 10 c.c. of freshly distilled hydrøiodic acid (sp.gr.1.653) were then added and the whole thoroughly mixed and kept in a thermostat for 4 hours.

The liberated iodine was estimated by titration with standard sodium thiosulphate solution.

The results are summarised in the following table where under t the actual reduction time in minutes and under x the percentage reduction is given. The latter is calculated from the equation :



W represents the weights.

The results are as follows:

α -bromo naphthalene/

	t in hours	W	X %
α -bromo naphthalene	4	0.091	4.5
β - " "	4	0.163	0.0
α - iodo naphthalene	4	0.193	62.0
β - " "	4	0.173	7.0
α - naphthol	4	0.171	0.0
β - naphthol	4	0.170	0.0

In order to ascertain if iodine is liberated by influences others than that of the hydroiodic acid (such as $2 R CH_2 I \rightarrow R CH_2 CH_2 R + I_2$) special experiments were carried out.

α - and β - iodo naphthalene were dissolved in glacial acetic acid and placed in the thermostat at 100° under the same conditions as the reductions carried out before, except that no hydroiodic acid was added, but it was found that α - and β - iodo naphthalene did not undergo change under these conditions.

The concentration of the hydroiodic acid and to a smaller extent the amount of free iodine in it, both influence the rate of reduction and therefore a series of reductions were as far as possible carried out on the same day and with the same hydroiodic acid.

As iodine is slowly ~~deliberated~~ from a solution of hydroiodic acid on account of atmospheric oxydation, a blank experiment was carried out at the same time and connections applied in each case.

For/

For temperatures between 25° and 100° boiling vapour thermostats have been employed. The glass stoppered measuring flask, containing the compound to be reduced in glacial acetic acid solution and hydroiodic acid, was immersed for a definite period of time in the vapour of the liquid, which was boiling in a wide necked flask, fitted with a reflux condenser. Any desirable temperature may be obtained in this way by the choice of a liquid of a suitable boiling point. Reductions at 100° were also carried out in a glycerin bath, kept at this temperature, when a large number of experiments could be accomplished at once.

Reduction of the mono halogenated phenols by means of hydrø iodic acid.

Approximately 0.17 gm. of the three hydroxy-bromo naphthols prepared, was dissolved in 15 c.c. of glacial acetic acid and to each solution, placed in a 25 c.c. glass stoppered measuring flask, 5 c.c. of constant boiling hydrø iodic acid added. The whole was then carefully mixed and placed in a thermostat at 75° (vapour of boiling carbon tetrachloride). The liberated iodine was estimated as before. By this method, reduction curves from 2-I; I-4 and I-5 hydroxy-bromo naphthol were obtained:

				t min.	x %
2	hydroxy-I-bromo	naphthol		15	95
I	" -4-	" "		15	94
I	" -5-	" "		60	6

w, t and x have the same significance as before.

On account of the rapid reduction of the 2-I and I-4 hydroxy-bromo naphthol under these conditions, both were reduced at 25°, the comparison is as follows.

<u>2-Hydroxy-I-bromo naphthol</u>			<u>I-Hydroxy-4-bromo naphthol</u>		
w	t min	x%	w	t min	x%
0.17 gm.	15	36	0.177	15	15
	30	63		30	27
	45	76		45	38
	90	96		90	62
	120	100		120	72

I:6-Dibromo- β -naphthol (Proc. chem.Soc. 1889,71) and ortho and para bromo phenol were reduced under the same conditions.

I:6-Dibromo- β -naphthol

w	t min	x%
0.179	15	9
	30	17
	45	24
	90	44
	120	54

ortho/

<u>ortho bromo phenol</u>			<u>para bromo phenol</u>		
w	t min	x%	w	t min	x%
0.17	30	2.7	0.17	30	2.5
	60	5.0		60	3.8
	120	7.1		120	5.0

These tables are graphically represented in figure II page 66.

Hydrolyses of

α - and β -naphthyl methyl bromide

1-bromo- β -naphthyl methyl bromide and

4-bromo- α -naphthyl methyl bromide

5-bromo- α -naphthyl methyl bromide.

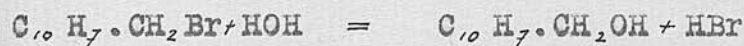
The hydrolyses of these compounds were carried out at 25°. The hydrolysing agent used was 90 per cent aqueous alcohol. At this temperature hydrolysis proceeded very slowly and were also carried out at 60°.

Hydrolysis at 25°.

Each compound (0.5 gm. approx.) in a 100 c.c. standard flask was dissolved in 90 c.c. absolute alcohol. The solution 10 c.c. of distilled water were added and after the whole had been thoroughly mixed, the flasks were placed in a thermostat at 25°. Ten c.c. of this solution were with drawn from time to time, poured into excess of water and the free hydro bromic acid estimated by titration with standard/

standard ammonium hydroxide solution, methyl red being used as indicator.

In the following tables t represents the time from the commencement of the experiment and x the percentage of hydrolysis, calculated from the equations:



and



whilst w is the weight in grams used.

<u>α-Naphthyl methyl bromide.</u>		<u>β-Naphthyl methyl bromide.</u>	
w 0.502 gm.		w 0.565 gm.	
t in hours	x%	t in hours	x%
24	37	24	27
48	59	48	45
72	73	72	60
96	82	96	70
120	87	120	78
168	93	168	87
240	97	240	93
312	98	312	97

For/

For comparison the hydrolysis of benzyl bromide is given here:

Benzyl bromide.

t hours	x%
24	17
48	30
72	41
96	51
120	59
168	70
240	81
312	86
364	88

1-bromo- β -naphthylmethyl bromide.

w 0.503 gm.

t hours	x%
48	16
96	31
144	42
192	51
240	59
312	68
364	74

4-bromo- α -naphthylmethyl bromide.

w 0.512 gm.

t hours	x%
48	33
96	59
144	76
192	83
240	86
312	89
364	90

5-bromo- α -naphthylmethyl bromide.

w 0.162 gm.

t hours	x%
6	4
48	18
96	52
144	68
240	79

Hydrolysis at 60°.

Twenty c.c. of a standard solution of the bromides in absolute alcohol (102 c.c.) were placed in a standard 25 c.c. flask, 5 c.c. of water added and the volume was made exactly 25 c.c. by the addition of absolute alcohol. The whole was thoroughly mixed and the flask then immersed in the vapour of boiling chloroform for a definite interval of time.

The contents of the flasks were washed into excess of water and the free hydro bromic acid titrated by a standard solution of ammonium hydroxide as before. In the following table, t and x have the same significance as before.

α -naphthyl methyl bromide. β -naphthylmethyl bromide

t hours	x%	t hours	x%
$\frac{1}{2}$	49	$\frac{1}{2}$	32
1	72	1	50
2	91	2	75
4	97	4	92
8	99	8	94

1-bromo- β -naphthyl methyl bromide. 4-bromo- α -naphthyl methyl bromide.

t hours	x%	t hours	x%
$\frac{1}{2}$	10	$\frac{1}{2}$	20
1	18	1	37
2	29	2	57
4	48	4	82
8	73	8	94

For comparison the hydrolysis of benzyl bromide at 60° is given here.

(J.C.S., 1926, 124, 221.)

w 0.461 gm	t hours	x%
	$\frac{1}{2}$	22
	1	39
	2	59
	4	80
	8	88

Hydrolysis of

4-Methoxy- α -naphthyl methyl bromide and

5-Methoxy- α -naphthyl methyl bromide.

Each of these compounds in 25 c.c. standard flasks were dissolved in absolute alcohol (0.06 gm. in every 10 c.c.). To the solutions distilled water was added to produce 90% aqueous alcohol and after the whole had been thoroughly mixed, the flasks were placed in a thermostat at 25°. Five c.c. of this solution were withdrawn immediately after the addition of the water and *adequat* portions of the remainder after definite intervals of time. The free hydro bromic acid was again estimated by titration with standard ammonium hydroxide solution as before.

4-Methoxy/

<u>4-Methoxy-α-naphthyl</u>		<u>5-Methoxy-α-naphthyl</u>	
<u>methyl bromide.</u>		<u>methyl bromide.</u>	
t mins.	x%	t hours	x%
5	80	3	10
	*	24	50
		48	73
		96	87

Samples of the titrated 1:5 compound were heated for a short time on the steam bath, when hydrolysis went almost to completion. (90%)

Sufficient 1:5 derivative was not obtained for reduction experiments and Lapworth and Shoesmith (J.C.S., 1922, 121, 1391) have established the non-reducibility of p-methoxy benzyl bromide, so owing to the similarities between this and the 1:4 compound the latter was not reduced.

Reduction of

1-Bromo- β -methyl naphthalene and

4-Bromo- α - " " "

Approximately 0.17 gm. of these compounds were weighed out in 25 c.c. standard flasks and dissolved in 10 c.c. glacial acetic acid. Ten c.c. of freshly distilled hydrø iodic acid (sp.gr. 1.652) were then added and kept in a thermostat at 100° for 2, 4 and 6 hours. The liberated iodine was estimated by titration with sodium/

* The sample used here was one of 80% purity. It probably crystallises with benzene of crystallisation.

sodium thio sulphate solution as before.

The results are summarised as follows:

1-Bromo- β -methyl
naphthalene.

t hours	x%
2	60
4	78
6	88

4-Bromo- α -methyl
naphthalene.

t hours	x%
2	29
4	50
6	62

Figure II.

REDUCTION

of

Bromo-naphthols and Bromo phenols
with hydriodic acid.

Temperature: 25°.

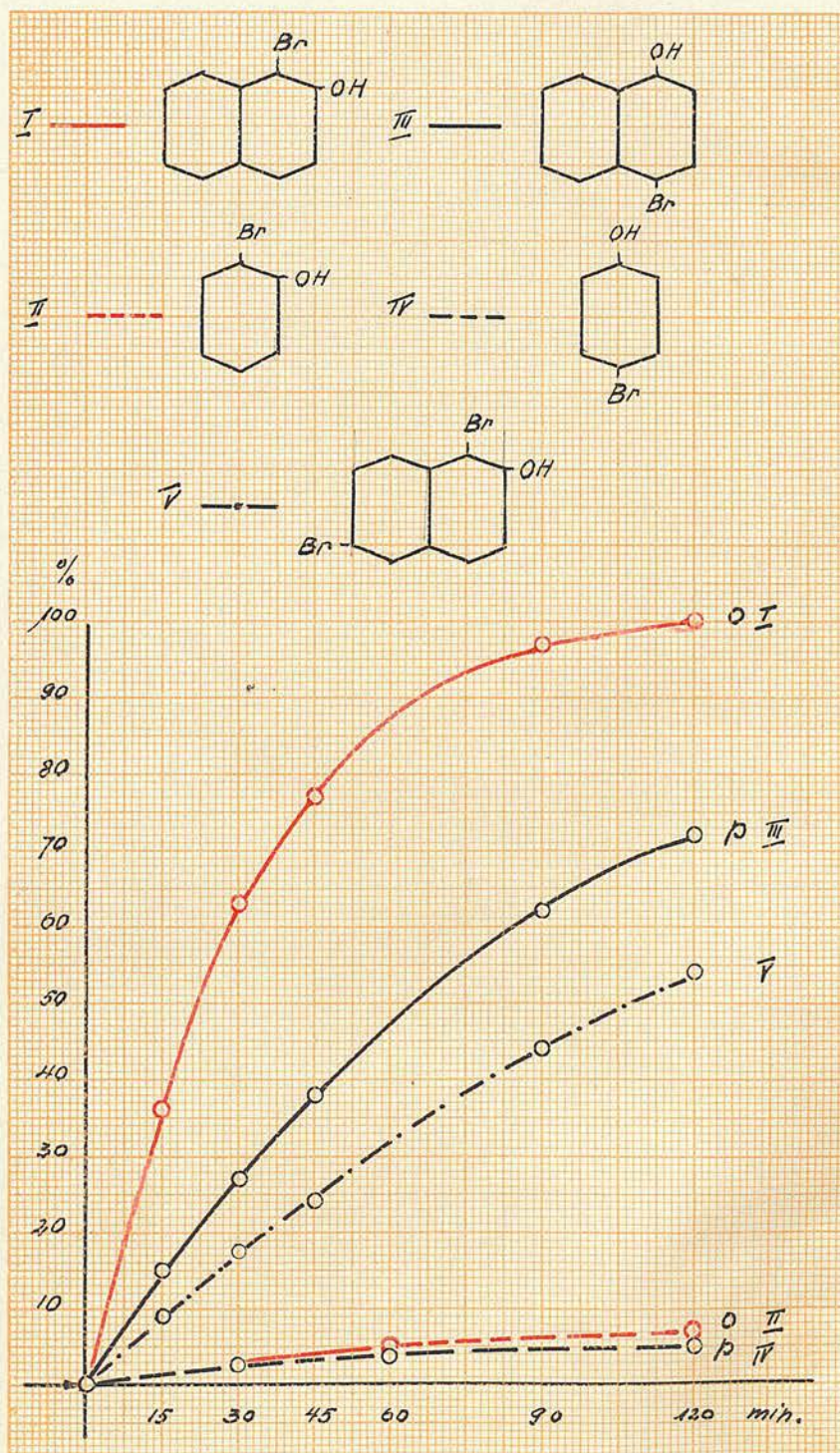


Figure III.

REDUCTION

of

1-Bromo- β -methyl naphthalene and 4-Bromo- α -methyl
naphthalene
with hydroiodic acid.

TEMPERATURE: 100°.

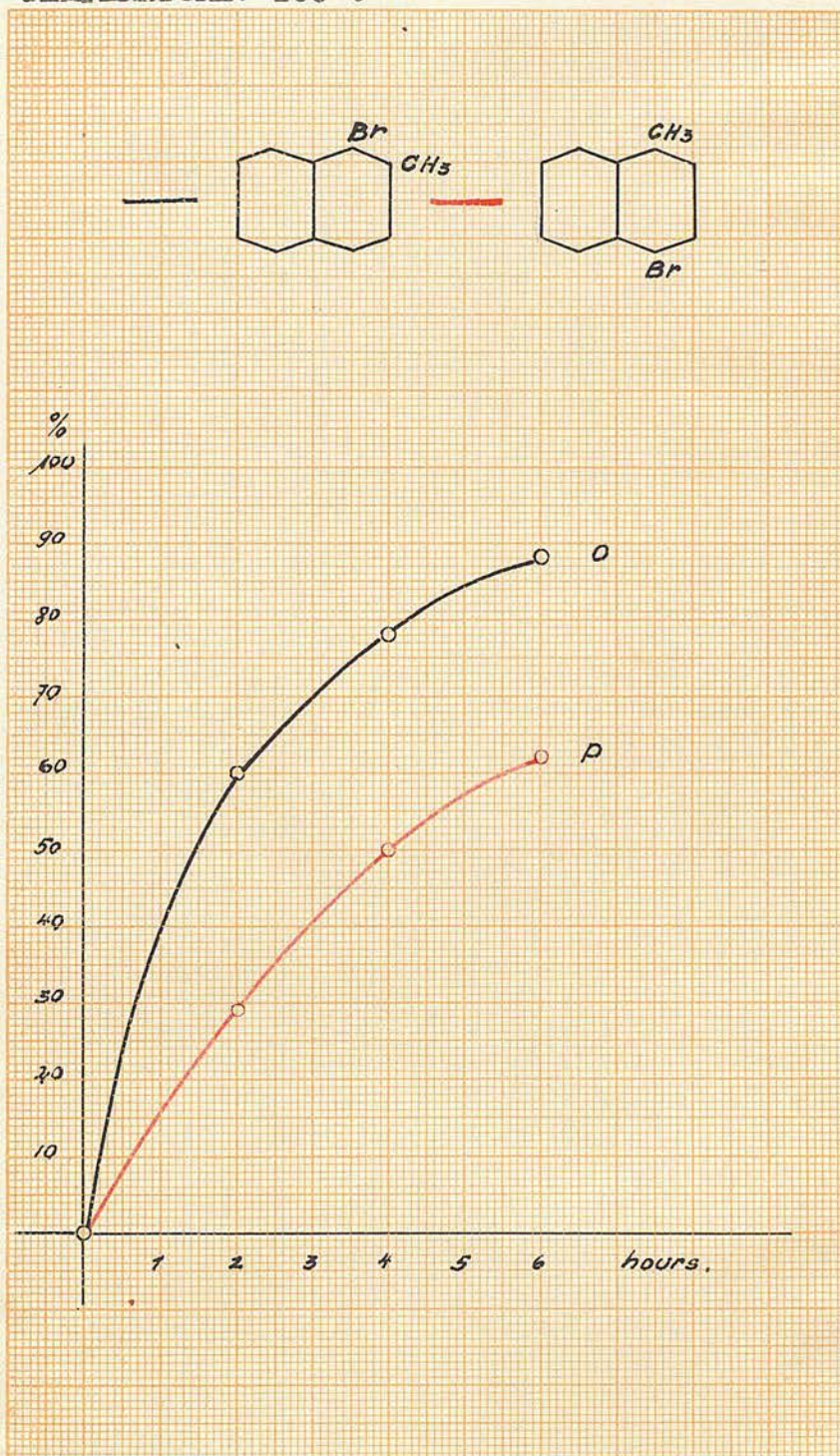


Figure IV.

REDUCTION

of

α - and - β -Naphthyl methyl bromide with hydroiodic acid.

TEMPERATURE: 77°.

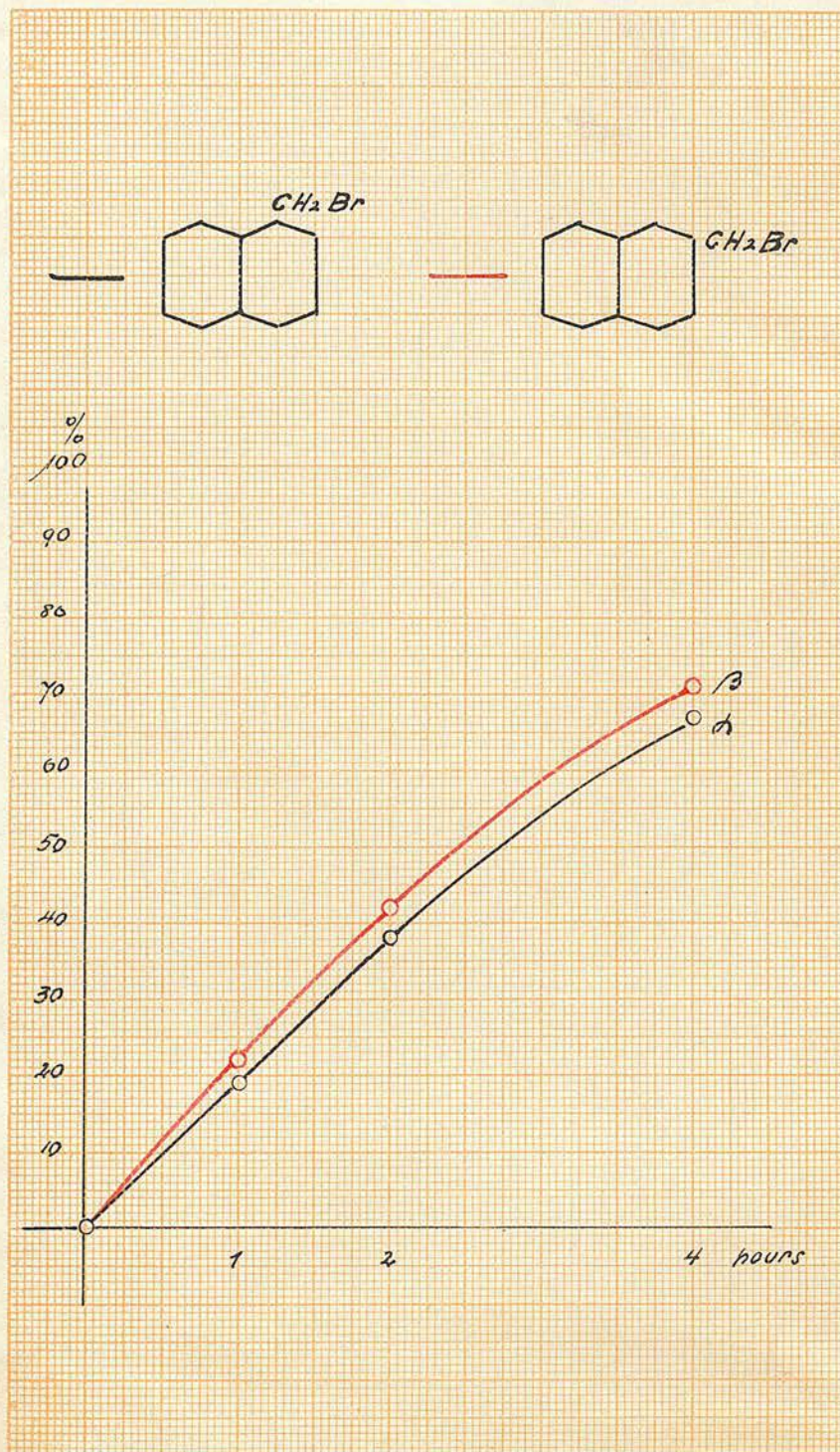
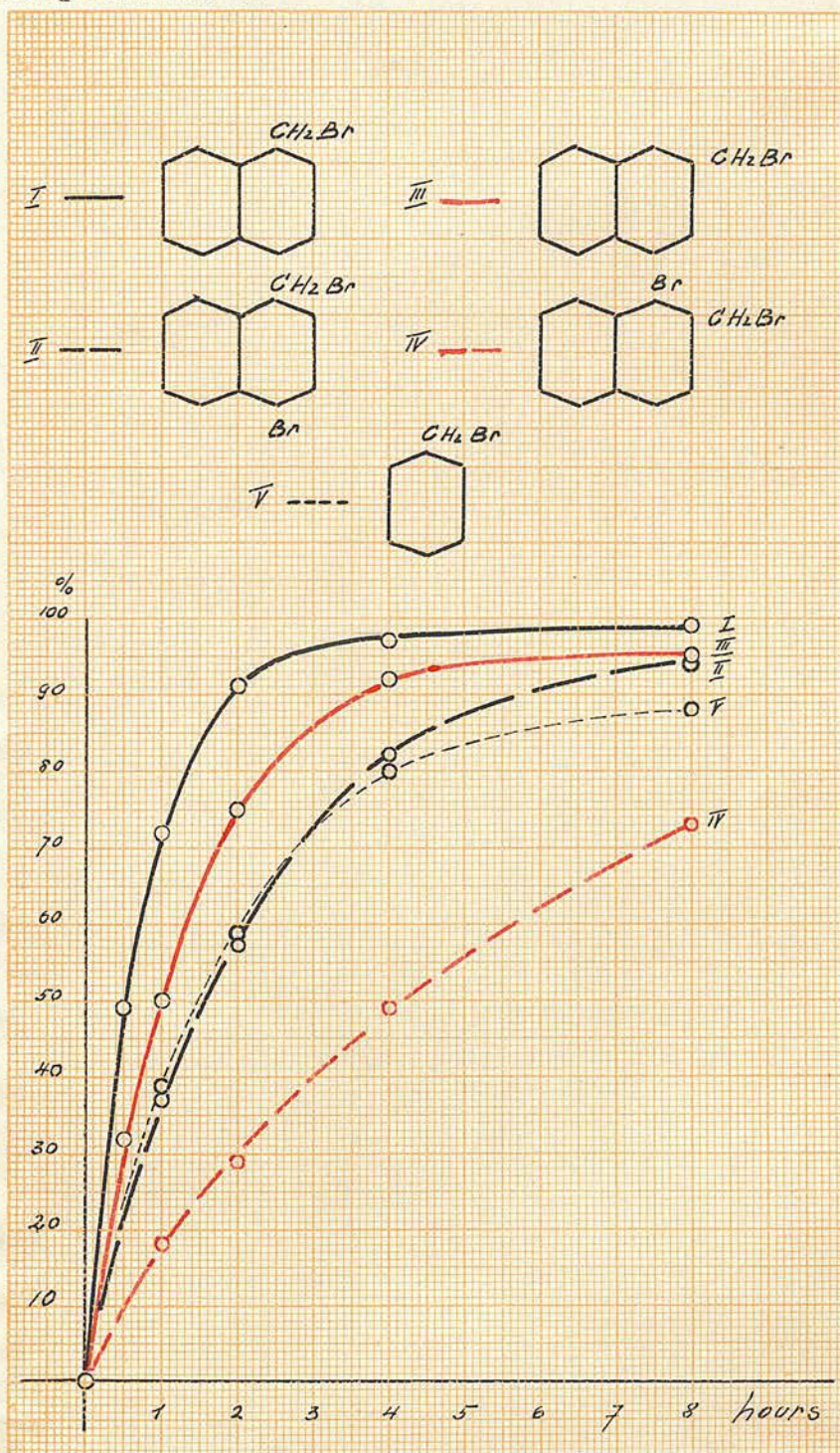


Figure V.

HYDROLYSIS
of

α and β naphthyl methyl bromide 1:2 and 4:1 bromo-
naphthyl methyl bromide and benzyl bromide.

Temperature 60°



TEMPERATURE 25°.

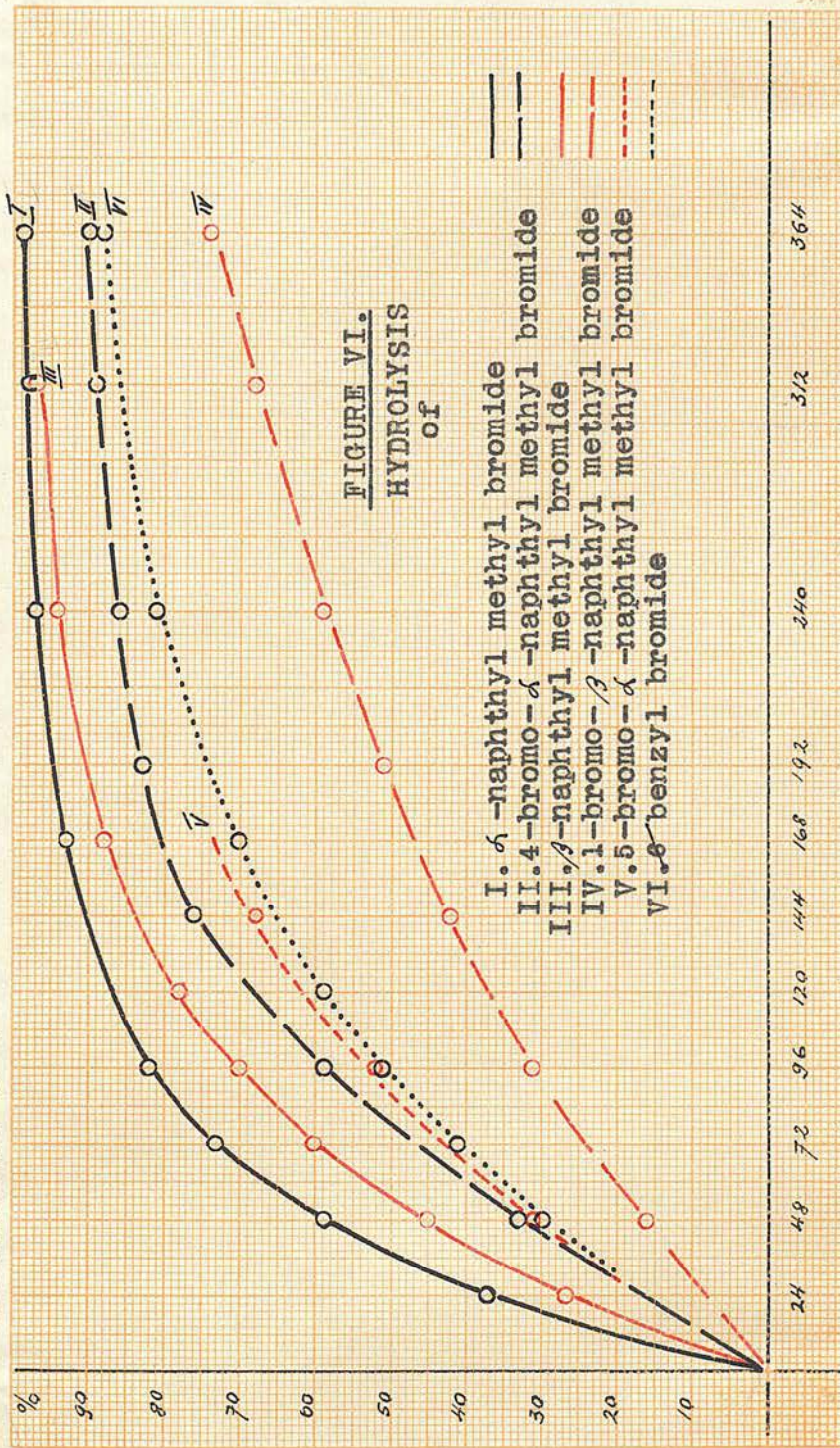
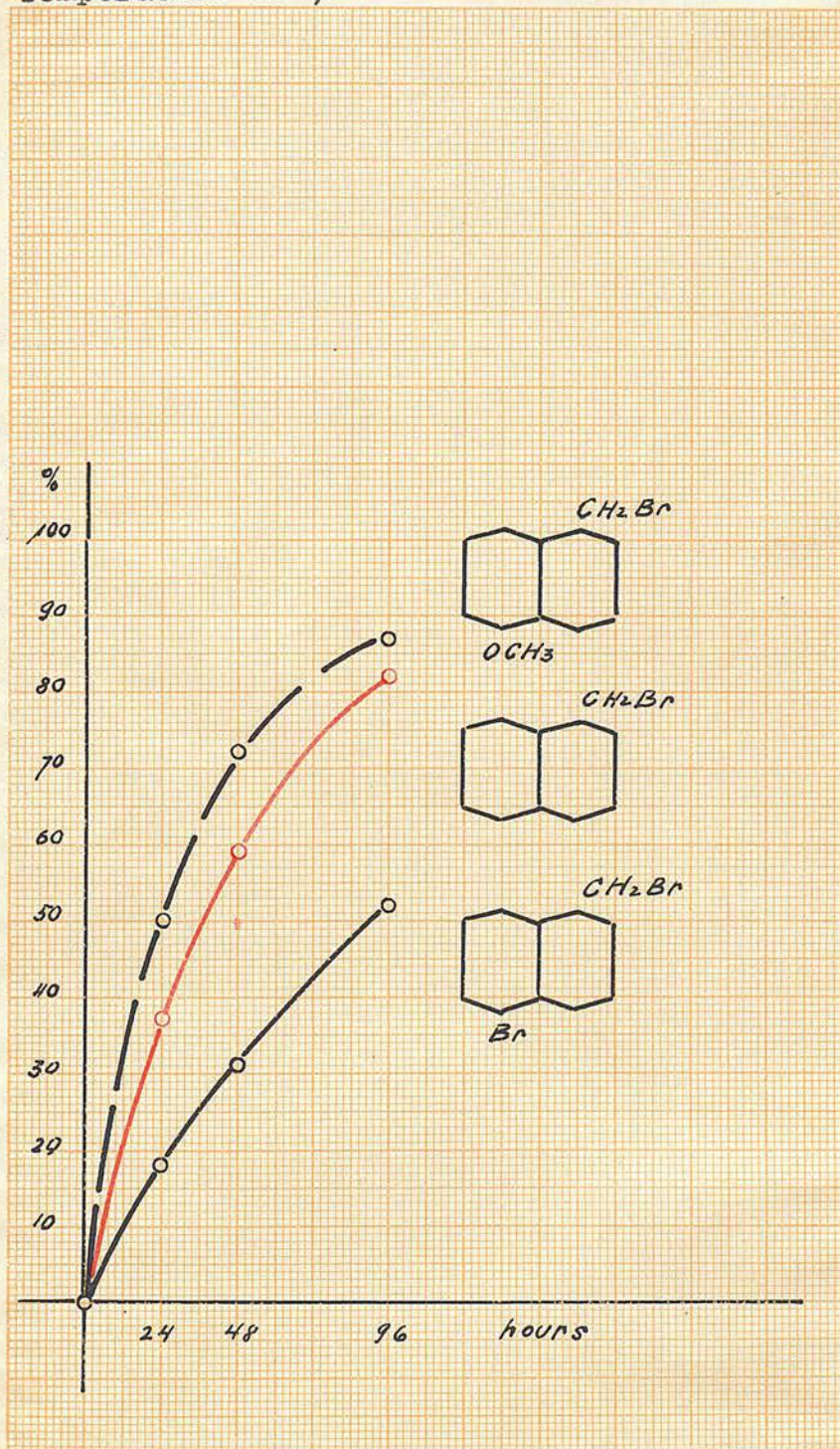


FIGURE VII.

Comparison of the Hydrolyses Curves.

of
 α -naphthyl-methyl bromide5-methoxy- α -naphthyl methyl bromide (red)5-bromo- α -naphthyl methyl bromide

Temperature 25°,



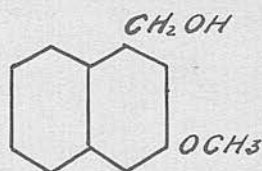
DISCUSSION OF RESULTS.

It is now generally admitted by chemists that the influences determining the reactivity of an atom in an organic molecule may be grouped under three heads, namely a. steric or structural influences, b. general polar influences and c. induced polar influences (vide Lapworth and Shoesmith J.C.S., 1922, 121, 1391). The steric or structural effects are generally apparent in aromatic organic compounds when the substituents are in ortho position to one another.

The general polar effect however is due to the influence of the substituent on the molecule as a whole (compare Lapworth, Mem. Manchester Phil. Soc., 1920, 67, No. 3, Kermack and Robinson J.C.S., 1922, 121, 427; Ann. Reports 1922, 19, 98.)

The present investigations have been successful in showing how two of these influences, namely the general and steric, affect reactivity in the naphthalene molecule.

It was not possible to judge the magnitude of the third effect i.e. the alternating effect, because of the somewhat unexpected difficulties of preparing 1:3 and 1:6 derivatives in the naphthalene series. It must be noted that the methods of preparing the carbinol of the 1:3 compound/



compound have been carefully worked out and the starting material for 1:6 and 1:7 derivatives, namely 6 methoxy-naphthoic acid and 7-methoxy-naphthoic acid has also been

prepared. Time did not permit the long repetitions necessary for the preparation of the 1:3 derivative in a quantity, sufficient to prepare the bromide.

In general however, it may now be stated that when we have the substituents in the same ring the reactivities are almost comparable with those already noted in the benzene series. There are however several very important differences between naphthalene and the corresponding benzene derivatives to be especially noted, namely the rapid reduction of 1-bromo- β -naphthol and the reduction of 1-bromo- β -methyl naphthalene and 4-bromo- α -methyl naphthalene. A suggestion as to why this is so is put forward later.

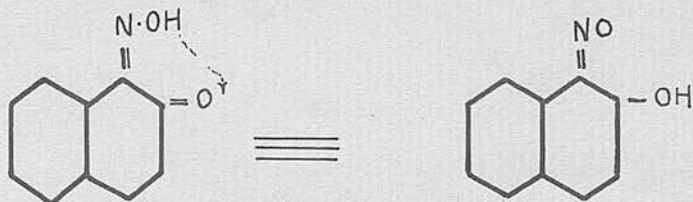
The transmission of an influence from one ring to another is apparent from

- a. the slight reducibility of 5-bromo- α -naphthol, an effect due to the hydroxyl group;
- b. the slow reduction of 2,6-dibromo- β -naphthol, an effect due to the bromine atom;
- c. the slow hydrolysis of 5-bromo- α -naphthyl methyl-bromide also due to the bromine atom and
- d. the hydrolysis of 5-methoxy- α -naphthyl methyl bromide/

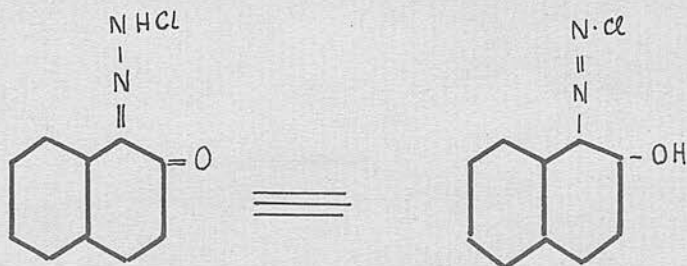
bromide, more rapid than that of the unsubstituted compound due to the presence of the methoxy group.

Enhanced reactivity due to Tautomerism.

One of the most note worthy phenomena met with here is the great reactivity towards hydrø iodic acid of α nuclear bromine when in ortho and para position to a hydroxyl or a methyl group, especially is this so in the 1:2 derivatives. Tautomeric modification are well known to be more prevalent in the naphthalene series than in the benzene series and again more prevalent in 1:2 than in 1:4 derivatives as e.g. the identity of α -nitroso- β -naphthol and oxime of naphthoquinone.



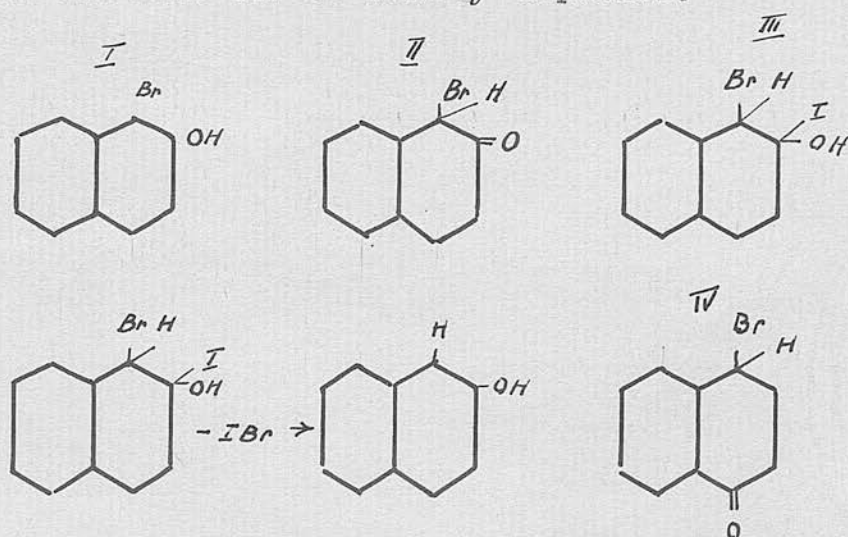
and azobenzene- β -naphthol and phenyl-hydrazone of naphthoquinone.



In/

In the benzene series p-quinonoid forms are recognised to be more stable than ortho quinonoid forms but in the naphthalene series the reverse is the case.

In this way it is readily apparent that 1-bromo- β -naphthol (I) would more easily give the ketonic tautomer (II) than the isomeric 4-bromo- α -naphthol would give (IV). In presence of hydriodic acid the unstable intermediate product (III) would be produced and lose IBr to form β -naphthol.

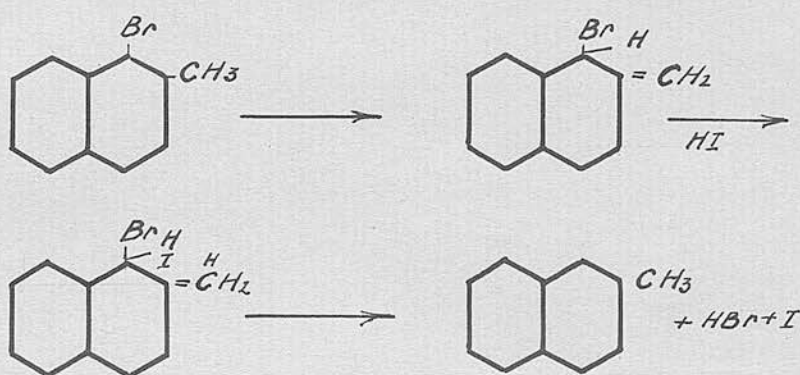


The greater reluctance of the 1:4 compound to assume the tautomeric form (IV) would account for its greater stability towards hydriodic acid.

In the benzene series p-bromo phenol is more unstable than the ortho isomeride, but far more stable than either of the naphthols examined, whilst 4-iodo resorcinol, a compound which would readily react in its keto form, is reduced immediately by hydriodic acid (Shoesmith, Hetherington and Slater, J.C.S., 1924, 124, 1312). On these lines the differences between the bromo-naphthols and bromo phenols are explicable.

The importance of the above thesis is recognised when we examine the reactivities of the bromo methyl naphthalenes of the formula $\text{Br} \cdot \text{C}_{10} \text{H}_6 \cdot \text{CH}_3$. The 1:2 and the 1:4 isomerides are compounds in which a nuclear bromine atom has been rendered labile towards hydroiodic acid by the presence of a CH_3 group, a phenomenon not paralleled in the benzene series and one, which is of great importance as it should lead to the preparation of various bromo- β -methyl naphthalenes (via further brominated compounds after removal of the labile bromine by hydroiodic acid) on the same lines as those already employed by previous workers, in the investigation of 6-bromo-2-naphthol.

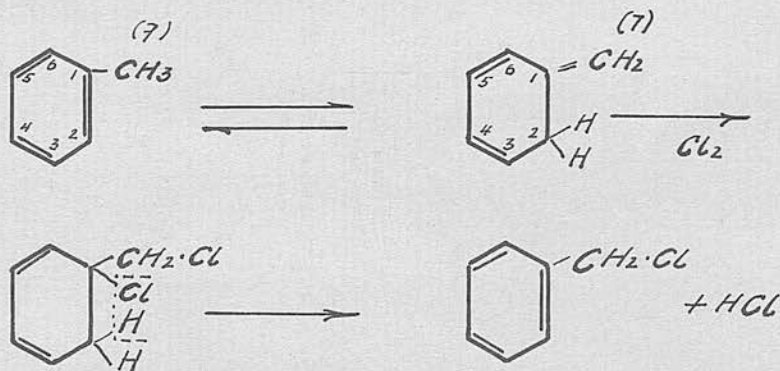
Here again, the ease of reduction of the bromo derivatives by hydroiodic acid must be due to the presence of a ketonic form, as represented in the following diagram.



That toluene does exist at a higher temperature in a similar form has been recently postulated by/

by Schorigin (Ber., 1926, 59, 2502) especially with regard to the substitution in the side chain of aromatic compounds (vide also Barnett and Matthews, Ber., 1926, 59, 1429). Substitution in the side chain of toluene by Halogen, NO_2 , OH oxydation etc., is explained by assuming tautomeric forms as represented in the following diagrams.

The second, apparently more reactive form is produced by importation and increase of energy in reactions, taking place under the influence of higher temperature, ultra violet light, etc. It is assumed that the entering molecules are primary attached to the double bond (1:7)



and in the second phase of the reaction, the unstable addition compound decomposes and thus the normal position of the double bonds in the benzene nucleus is readjusted.

The authors discovered that the optical properties of toluene at high temperature are in accordance with such a view. The greater tendency of tautomers to exist in the naphthalene series would/

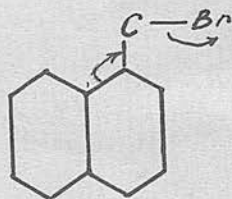
would thus account satisfactory for the great reactivity of bromo-methyl naphthalenes.

There is a big difference between the rate of reduction of the 1:2 and 4:1 bromo naphthol and the 1:5 isomeride. This bears out the suggestions on which the discussion of the reactivity of the isomerides in the first ring are based, since the existence of a similar tautomeric form is not to be expected in the 5-bromo- α -naphthol, which would account for its greater stability towards hydroiodic acid. It is evident however that in this case, the general effect is transmitted to a certain extent from the first ring to the second, the hydroxyl group in 1 position thus influencing slightly the bromine atom in 5 position.

Rapid hydrolysis of α naphthyl methyl bromide.

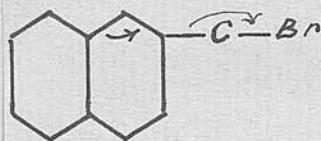
The rapidity with which α -naphthyl methyl bromide is hydrolysed as compared with the β isomeride is a further example of the rule, quoted recently by Shoesmith and Taylor (J.C.S., 1926, 127, 2832) which was first propounded by Olivier (Rec. trav. chim., 1923, 42, 775). The rule, ^{which} is of fairly general application is as follows: in a series of isomeric benzyl halides, those isomerides in which the $-\text{CH}_2\text{Hal}$ group is attached to ~~the~~ ^{the} carbon atom of the benzene nucleus, which is attacked during substitution of the corresponding/

corresponding benzene derivative, are the ones, from which halogen is most readily removed by aqueous alcohol as hydrolysing agent. As is well known, up to temperatures of about 60° substituents enter the naphthalene molecule in α position and α -naphthyl methyl bromide is more rapidly hydrolysed than the β isomeride. The compound is remarkably readily hydrolysed and the ultimate cause must be regarded as due to the unstability of one of the central electron octets (Kermack and Robinson, J.C.S., 1922, 121, 427), which would result in a condition of affairs represented by the following diagram, the heaping up of



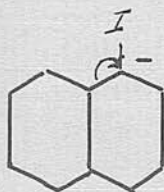
electrons on the terminal bromine atom rendering it extremely readily removed as bromide ion. In the β -isomeride, the conditions ruling are represented as follows, which means that the C-Br linkage would now be

stronger than in the α -isomeride. The heaping up of electrons on the terminal bromine atom in all readily hydrolysed halides is doubtless the



potent factor governing their reactivity towards a hydrolysing agent, as will be seen in the methoxy-naphthyl methyl bromides which follow.

The great reactivity of α iodo naphthalene towards hydroiodic acid is probably due to the same cause, the carbon atom becoming extra ordinarily negative. The great inherent "positivity" of iodine compared with bromine accounts for the stability of the bromo compound.



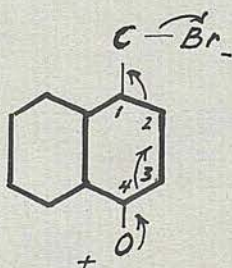
of iodine compared with bromine accounts for the stability of the bromo compound.

Rapid hydrolysis of 4-methoxy- α -naphthyl methyl bromide.

It was pointed out in the introduction that an influence is transmitted from one ring to another, but the difference of reactivity observed by hydrolysing 4-methoxy- α -naphthyl methyl bromide and

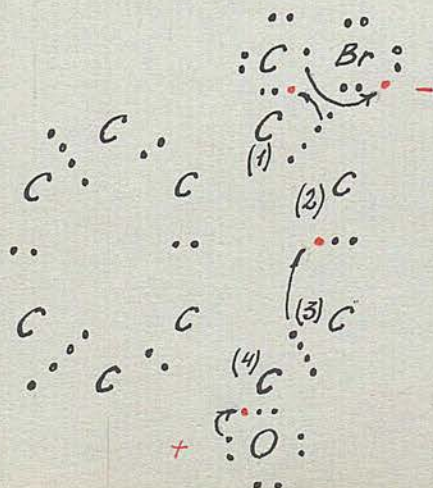


shows that the transmission is much more effective when carried through carbon atoms which are all in the same ring. The great lability of the bromine atom in the 1:4 compound is exactly what would have been expected from considerations of electron displacement (Robinson, J.C.S., 1926, 128, 401) or the stability of electron octets (Robinson and Kermack, J.C.S., 1922, 121, 427) as is seen from the diagram. In accordance



with Robinson's views the electrons are regarded as moving from the oxygen atom, in the manner denoted by the arrows. Explained more

fully, it will be seen from this figure that the 4 carbon atom becomes surrounded by 9 electrons and in



order to rebuild its stable 8 electron shell a ~~one~~ electron passes along the nucleus between the carbon atoms in 2 and 3 position, the disturbance/

disturbance being repeated ^{at} ~~in~~ C₂. The process goes forward until finally the electrons forming the usual co-valency between C and Br are diminished and the bromine atom is then readily removed by means of a hydrolysing agent.

If the same mechanism of displacement of electrons applies in 5-methoxy- α -naphthyl methyl bromide, that is to say if the disturbance of the electronic equilibrium is caused by the oxygen attached to the nucleus carbon in 5 position the effect should be some what similar. The electron shift from the 5 to the I position is a process which evidently does not take place so readily as from the 4 to the I owing to the peculiar position of the two central carbon atoms, which would necessitate the transmission of the influence via 6 or 4 position, around the nucleus. Although this should not weaken the transmission to the extent as is proved by the experiment, it must be something of this nature which is causing the big difference in reactivity between I:4 and I:5 isomerides. It may be however, that only a general effect is transmitted from the 5 to the I position, a suggestion born out by the behaviour of the 5-bromo- α -naphthyl methyl bromide where the general effect is marked.

The action of 4-methoxy- α -naphthyl methyl bromide towards aqueous alcohol makes it evident that a close relationship exists between this and the corresponding/

corresponding compound in the benzene series, namely p-methoxy-benzyl bromide. As already stated in the experimental part, 4-methoxy- α -naphthyl methyl bromide was at once completely hydrolysed when brought in solution in aqueous alcohol. Lapworth and Shoesmith (J.C.S., 1922, 121, 1398) found that the extremely high speed at which alkalis act on the ortho and para methoxy-benzyles bromides did not render it possible to measure the reaction velocity in dilute alcohol at 25°. Even when only aqueous alcohol was used hydrolysis was almost completed after 5 minutes a result similar to that found by hydrolysing 4-methoxy- α -naphthyl methyl bromide.

4-methoxy- α -naphthyl methyl bromide as well as p-methoxy benzyl bromide ~~fumed~~ in the air and decomposed very quickly.

Bromo-naphthyl methyl bromides.

The order of reactivity of the bromo-naphthyl methyl bromides is, unsubstituted α -naphthyl methyl bromide > 4-bromo- α -naphthyl methyl bromide > 5-bromo- α -naphthyl methyl bromide and unsubstituted β -naphthyl methyl bromide > 1-bromo- β -naphthyl methyl bromide.

It is thus shown that a. / bromine has a considerable general effect from the 4 and the 5 position i.e. the general effect is transmitted through both rings and b. / the non reactivity of the 1:2 derivative is due to causes already noted by Shoesmith and Slater (J.C.S., 1926, 127, 214) in the benzene series. It was there pointed out that this is probably not steric effect in the general accepted sense, a conclusion arrived at also by Oliver (Rec. trav. chim., 1923, 42, 775) a few months later.

The most interesting point in this series is the marked diminution in the reactivity caused by a bromine atom in 5 position which is greater than that caused by a bromine atom in 4 position but this is in accordance with the substitution hydrolysis rule already referred to on page 78 . It is however a remarkable fact that bromine introduced into a naphthalene molecule should render the bromides so unreactive towards a hydrolysing agent, and with our ~~the~~ present knowledge it is difficult to say why it should /

the ring in which they are present (c.f. the great reactivity of the 1:4 methoxy benzyl compounds) and substitution takes place in the same ring. It can with confidence be prophesied that 4-nitro- α -naphthyl methyl bromide and 4-carboxy- α -naphthyl methyl bromide would lose their bromine with great difficulty in aqueous alcohol.

It is finally of interest to note the views of Scheribe (Ber., 1926, 59, 2664) who has been able to confirm the theory of the directing influence of positive and negative groups in benzene substitution on a purely physical basis, i.e. the absorption spectra of various substituted benzene derivatives.

Much more work remains to be done on similar lines in the naphthalene series but as will be seen from the foregoing a large number of interesting points have arisen all of which can be classified and examined quite satisfactorily when considered in the light of previous investigations.

SUMMARY.

The investigations have shown that in naphthalene compounds

- a. An influence is transmitted from one ring to the other.
 - b. The behaviour of substituted aryl methyl bromides in the naphthalene series when substituents are present in the same ring, is markedly similar to that of the corresponding compounds in the benzene series.
 - c. Slight differences exist between the two series in the case of nuclear substituted halogen derivatives but, these are easily explicable by a theory based on the existence of tautomeric modifications in the naphthalene series.
 - d. All the hydrolyses recorded are in accordance with the suggestion of Olivier, regarding the rates of hydrolysis of the bromides and substitution in the naphthalene nucleus.
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