15. *The Synthesis of Nine Chloroiodonaphthalenes.*

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Of the fourteen possible chloroiodonaphthalenes, two only have been reported. 1-Chloro-2-iodonaphthalene (Mascarelli and Martinelli, *Atti R. Accad. Lincei*, 1915, **24**, ii, 25) was prepared from 1-nitro-2-aminonaphthalene by diazotisation and subsequent treatment with potassium iodide in the presence of sulphuric acid. Willgerodt and Schlosser (*Ber.*, 1900, **33**, 693) claimed to have isolated 1-chloro-4-iodonaphthalene as one of the decomposition products of 1-iodonaphthalene dichloride ($C_{10}H_7ICl_2$) and described it as a yellow oil boiling above 300°.

By the controlled action of chlorine, bromine, and iodine on an organomercuric halide, or a mercury-bis-compound, the chloro-, bromo-, and iodo-compounds may be synthesised. The preparation of the iodo-derivatives is, however, unaccompanied by the danger of simultaneous direct halogenation of the nucleus, which, especially in the case of naphthalene, may attend the use of chlorine and bromine.

In the present investigation we have prepared nine chloroiodonaphthalenes (1-chloro-4-iodo- and 1-chloro-8-iodo-naphthalene in considerable quantity) and find all to be light-coloured, crystalline solids. The constitutions assigned are concluded from the structures of the intermediates used and the reactions employed.

The initial materials were commercially available aminonaphthalenesulphonic acids of known constitution and the reactions used were as follows :

$$\begin{aligned}&NH_2{\cdot}C_{10}H_6{\cdot}SO_3Na \longrightarrow C_{10}H_6Cl{\cdot}SO_3Na \longrightarrow C_{10}H_6Cl{\cdot}SO_2Cl \longrightarrow\\&C_{10}H_6Cl{\cdot}SO_2H \longrightarrow C_{10}H_6Cl{\cdot}HgCl \longrightarrow C_{10}H_6ClI.\end{aligned}$$

The preparation and properties of the mercury derivatives employed have been previously reported (Beattie and Whitmore, *J. Amer. Chem. Soc.*, 1933, **55**, 1567).

2-Iodonaphthalene was prepared by the action of iodine on 2-chloromercurinaphthalene and 2-mercuribisnaphthalene and found to have the properties reported in the literature.

1-Chloro-4-bromonaphthalene was synthesised by the action of bromine on 1-chloro-4-chloromercurinaphthalene, and shown to be identical with a specimen made by the direct bromination of monochloronaphthalene. The preparation by the latter method entailed many crystallisations before a product having the desired properties was obtained.

A possible explanation of this is as follows: As well as the other isomeric derivatives of 1-chloronaphthalene formed simultaneously, there is also the possibility of the presence of bromo-derivatives of 2-chloronaphthalene. The monochloronaphthalene used was prepared by the direct chlorination of naphthalene—a method in which it has been recently shown (Britton and Reed, U.S. Pat. 1,917,822, July 11th, 1933) a considerable quantity of 2-chloronaphthalene (as much as 8%) may be formed.

The presence of the β-compound in 1-chloronaphthalene made by direct chlorination may also be one cause of the trouble experienced (Oakwood, private communication, 1931) in isolating pure 1-chloro-4-nitronaphthalene from the mixture obtained by the nitration of 1-chloronaphthalene.

With the above assurance that the halogens acted in the usual manner on the mercury derivatives, and that the mercury compounds had the structures assumed, we proceeded with the preparation of the nine isomeric chloroiodonaphthalenes.

EXPERIMENTAL.

The compounds described were prepared by the action of alcoholic solutions of iodine and sodium iodide on 1-chloro-4-, 1-chloro-5-, 1-chloro-6-, 1-chloro-7-, 1-chloro-8-, 2-chloro-1-, 2-chloro-6-, 2-chloro-7-, and 2-chloro-8-chloromercurinaphthalene. The sodium iodide assisted in the solution of the iodine and subsequently in dissolving the inorganic mercuric halides formed. The most rapid absorption of iodine took place with 2 : 1- and 1 : 8-compounds, and the slowest was with the 2 : 6-derivative.

The experimental details used for the preparation of 1-chloro-4-iodonaphthalene may be employed in isolating any of the other chloroiodonaphthalenes described in this work. The products were crystallised from methyl or ethyl alcohol. The percentages of the halogens given are the average of two determinations.

Although the action of bromine in an aqueous bromide solution was not tried, the action of iodine proceeded much more satisfactorily than that of bromine in carbon tetrachloride. The alcohol appeared to wet the organo-mercury compound much more than the carbon tetrachloride and when the latter was used the inorganic salts formed dissolved but little.

1-*Chloro*-4-*bromonaphthalene*.—To a stirred, boiling mixture of 1-chloro-4-chloromercurinaphthalene (8 g.) and carbon tetrachloride (100 c.c.) in a suitably equipped 500-c.c. flask, was added a solution of bromine (3·2 g.) in the above solvent (240 c.c.), during about 1·5 hours. The solution was run in through the condenser at the same rate as that at which the bromine colour faded in the refluxing mixture. The black insoluble solid that separated contained a small amount of unchanged 1-chloro-4-chloromercurinaphthalene, but was mainly inorganic salts of mercury. The whole was finally heated and stirred for 1 hour. The liquid was filtered hot and 265 c.c. of solvent were distilled from the yellow filtrate. The residual liquor on cooling gave a small quantity of nearly white solid (1·07 g.), which was discarded. The filtrate was evaporated to dryness, and the red solid obtained (3·3 g.) boiled (charcoal) with 50 c.c. of methyl alcohol. When filtered and cooled, this gave white needles of 1-chloro-4-bromonaphthalene, m. p. 66·5—67° [alone or mixed with a sample (m. p. 66·5—67°) obtained from the bromination of 1-chloronaphthalene].

1-*Chloro*-4-*iodonaphthalene*.—To a mechanically stirred, refluxing mixture of 1-chloro-4-chloromercurinaphthalene (7·95 g.) in alcohol (100 c.c.), a warm solution of iodine (5·05 g.) and sodium iodide (10 g.) in alcohol (200 c.c.) was gradually added, at about the same rate as the colour faded. Refluxing and stirring were continued for 1 hour and the mixture was then filtered hot and 110 c.c. of alcohol were removed by distillation. The residual liquor was cooled and stirred, and a large volume of cold water added. The yellow precipitate formed was washed with cold water, twice with sodium iodide solution (20%), and finally with water. The product crystallised (charcoal) from methyl alcohol in white leaflets or needles of 1-*chloro*-4-*iodonaphthalene*, m. p. 54·5° (yield, 386 g. or 90% based on the total made) (Found: Cl + I, 56·4. $C_{10}H_6ClI$ requires Cl + I, 56·3%).

1-*Chloro*-5-*iodonaphthalene*, white needles, m. p. 89°; yield, 73% (Found: Cl + I, 56·1%).

1-*Chloro*-6-*iodonaphthalene*, white needles, m. p. 57°; yield, 70% (Found: Cl + I, 55·8%).

1-*Chloro*-7-*iodonaphthalene*, white needles, m. p. 39°; yield, 63% (Found: Cl + I, 56·0%).

1-*Chloro*-8-*iodonaphthalene* (over 250 g. of this compound were prepared), pale yellow leaflets, m. p. 80·5°; yield, 84% (Found: Cl + I, 56·0%).

2-*Chloro*-1-*iodonaphthalene*, white leaflets, m. p. 63°; yield, 64% (Found: Cl + I, 56·1%).

2-*Chloro*-6-*iodonaphthalene*, nacreous plates from methyl alcohol, m. p. 141°; yield, 70% (Found: Cl + I, 56·0%).

2-*Chloro*-7-*iodonaphthalene*, obtained as pale yellow leaflets, m. p. 129°; yield, 70% (Found: Cl + I, 57·0%).

2-*Chloro*-8-*iodonaphthalene*, long white needles, m. p. 55·5°; yield, 71% (Found: Cl + I, 56·3%).

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