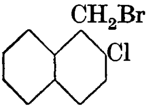
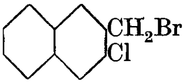
CCIV.—*Investigations on the Reactivity of Halogens in Various Types of Naphthalene Derivatives. Part II.*

By John Baldwin Shoesmith and Alexander Mackie.

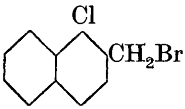
The investigations reported in Part I (J., 1927, 3098) have been continued, and the ease of removal by aqueous alcohol of the bromine in 2-chloro-1-naphthylmethyl bromide (I), 3-chloro- (II) and 1-chloro-2-naphthylmethyl bromide (III) examined. The bromine is removed at approximately the same rate from compounds (II) and



(I.)



(II.)



(III.)

(III), as is to be expected from the fact that the position of the chlorine atom in relation to the bromine is the same in both cases.

The removal of the bromine from 2-chloro-1-naphthylmethyl bromide takes place more readily than does that from (II) or (III), and in this respect the bromide behaves analogously to 2-methyl-1-naphthylmethyl bromide (J., 1927, 3099).

The compounds (I) and (II) were obtained by the following series of reactions,

$$C_{10}H_6Cl{\cdot}CHO \xrightarrow{KOH} C_{10}H_6Cl{\cdot}CH_2{\cdot}OH \xrightarrow{HBr} C_{10}H_6Cl{\cdot}CH_2{\cdot}Br,$$

and it was noted that 2-chloro-1-naphthaldehyde was reduced with much greater difficulty than 3-chloro-2-naphthaldehyde. In this particular instance, therefore, the hindering effect of the unsubstituted benzene nucleus and of the chlorine atom, both in ortho-positions to the aldehydo-group, was apparent. The acid formed, in addition to the carbinol, in this reduction was not the expected 2-chloro-1-naphthoic acid, m. p. 152—153° (Rabe, *Ber.*, 1889, **22**, 394), but 2-chloro-1-naphthylacrylic acid, the formation of which is analogous to that of 2 : 3-dimethoxycinnamic acid during the reduction of veratraldehyde with alcoholic potassium hydroxide (Perkin and Stoyle, J., 1923, **123**, 3173). This is the first instance of abnormal reduction in the present series of investigations.

EXPERIMENTAL.

1-*Chloro*-2-*naphthylmethyl Bromide*.—2-Methylnaphthalene was converted at room temperatures into 1-chloro-2-methylnaphthalene, and this with bromine vapour at 200° into 1-*chloro*-2-*naphthylmethyl bromide*. The crude bromide (which was prepared in lots of 3 g. to avoid tarring), after being pressed on porous tile, crystallised from alcohol in colourless prisms, m. p. 81° (yield, 50%) (Found : Br, 31·3. $C_{11}H_{10}ClBr$ requires Br, 31·3%).

2-*Chloro*-1-*naphthylmethyl Bromide*.—Considerable difficulty was experienced in the preparation of 2-chloro-1-naphthaldehyde (*Ber.*, 1911, **44**, 2099), which was finally obtained by heating 2-hydroxy-1-naphthaldehyde (3 g.) with phosphorus pentachloride (7·5 g.) at 165° for 3·5 hours. The reaction mixture was boiled with formic acid (100%) for 1 hour, diluted with water, and extracted with ether. The extract was shaken in turn with caustic soda solution and aqueous sodium bisulphite. The solid aldehyde bisulphite compound was collected and dissolved in warm water, and the aldehyde liberated with sodium carbonate. It crystallised from light petroleum in needles, m. p. 75°. The yield could not be made to exceed 0·5 g. Reduction did not proceed very readily and was finally brought about by warming the aldehyde to 75° with 66%

aqueous caustic potash to which a little alcohol had been added, allowing the mixture to cool to 18° and reheating it after 24 hours. The product when cold was poured into water, the solution extracted with ether, the extract washed with alkali, and the ether evaporated. 2-*Chloro*-1-*naphthylcarbinol*, thus obtained, crystallised from light petroleum in long prisms, m. p. 110° (Found : Cl, 18·0. $C_{11}H_9OCl$ requires Cl, 18·4%). The carbinol was dissolved in benzene, the solution *warmed to* 45°, and hydrogen bromide passed in; water separated after a time, and when the reaction was complete the solution was dried over a little calcium chloride, and the benzene removed. The residual 2-*chloro*-1-*naphthylmethyl bromide* crystallised from light petroleum in needles, m. p. 100·5° (Found : Br, 31·0%).

3 - *Chloro* - 2 - *naphthylmethyl Bromide*.—3-Chloro - 2 - naphthoyl chloride (*Ber.*, 1901, **34**, 4159) was reduced by hydrogen in presence of palladinised barium sulphate in xylene to 3-*chloro*-2-*naphthaldehyde*, which crystallised from light petroleum in stellate clusters of needles, m. p. 121° (Found : Cl, 18·6. $C_{11}H_7OCl$ requires Cl, 18·6%). The oxime formed fine white needles, m. p. 152°, from aqueous alcohol, the *p*-nitrophenylhydrazone scarlet needles, m. p. 263°, from acetic acid, and the semicarbazone feathery needles, m. p. 268°, from alcohol.

The aldehyde was converted by means of 66% aqueous potassium hydroxide (see above) into 3-*chloro*-2-*naphthylcarbinol*, which crystallised from light petroleum in needles, m. p. 111° (Found : C, 68·2; H, 3·8. $C_{11}H_9OCl$ requires C, 68·6; H, 3·6%). The carbinol in benzene solution with dry hydrogen bromide gave 3-*chloro*-2-*naphthylmethyl bromide*, which crystallised from alcohol in colourless rhombic plates, m. p. 97° (Found : Br, 30·8%).

The hydrolyses of the bromides were carried out in aqueous alcohol at 25° as described in the case of analogous compounds reported in Part I.

Compound.	$k \times 10^6$.	Mean $k \times 10^6$.
3-Chloro-2-naphthylmethyl bromide	71, 70, 70	70
1-Chloro-2-naphthylmethyl bromide	72, 73, 71	72
2-Chloro-1-naphthylmethyl bromide	80, 79, 80	80

The authors wish to acknowledge a grant from the Chemical Society, and a Carnegie Fellowship to one of them (J. B. S.) during the tenure of which the research was carried out.

EDINBURGH UNIVERSITY. [*Received, May 22nd*, 1930.]