CCCCVIII.—*Investigations on the Reactivity of Halogens in Various Types of Naphthalene Derivatives. Part I.*

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A SERIES of investigations has been undertaken with the view of extending work already carried out on halogenated derivatives of benzene (J., 1922, **121**, 1391; 1923, **123**, 2828; 1924, **125**, 1312, 2278; 1926, 214, 2832; this vol., p. 1768) to the naphthalene series. It has been discovered that the ease of replacement of both nuclear and side-chain halogen in naphthalene compounds is markedly different from that in the corresponding benzene derivatives; thus, α- and β-naphthylmethyl bromides are both more readily hydrolysed in aqueous alcohol at 25° than is benzyl bromide, the order of ease of hydrolysis being $\alpha > \beta$, a fact which substantiates the rule put forward by Olivier (*Rec. trav. chim.*, 1923, **42**, 775) showing the connexion between the rate of hydrolysis of benzyl halides and substitution in the aromatic nucleus. Owing to the rapidity of the hydrolysis, it was not possible to ascertain whether this order remained the same at higher temperatures, but it appeared to be so at 60°. The two isomerides are also almost equally more rapidly reduced than benzyl bromide at 77°.

Of the α- and β-bromo- and iodo-naphthalenes, only α-iodonaphthalene is appreciably reduced at 100° by hydrogen iodide, and it appears as if the halogen (especially iodine) attached to the nucleus in the position which is most readily attacked during substitution is correspondingly most readily removed by hydrogen iodide.

The reduction of 1-bromo-β-naphthol and 4-bromo-α-naphthol proved of interest in that (1) they are both very readily reduced, and (2) the order of ease of reduction is $o > p$, the reverse of the case in the corresponding benzene series. It has already been suggested (J., 1924, **125**, 1314) by one of us, and independently by Nicholet (*J. Amer. Chem. Soc.*, 1927, **49**, 1812), that the intermediate formation of molecules of a quinonoid type probably assists the reduction of such compounds, a suggestion borne out by the great reactivity of the ortho-compound above (since ortho-quinonoid forms are recognised as more prevalent in the naphthalene than in the benzene series), and also by the very slow rate of reduction of 5-bromo-α-naphthol in which the possibility of intervention of quinonoid formation is not so marked.

The formation of active quinonoid molecules is probably a powerful factor in the ease of reduction of the second series of nuclear-halogenated naphthalene derivatives examined,* *viz.*, 1-bromo-2-methylnaphthalene and 4-bromo-1-methylnaphthalene, both of which are reduced by hydriodic acid at 100°, in contradistinction to the bromotoluenes, which are stable, and the order is again 1 : 2 > 1 : 4.

In various substituted α-naphthylmethyl bromides the reactivity of the bromine atoms was in the decreasing order p-OMe > p-CH_3 > unsubs. > p-Br, which is the same as in the hydrolysis of substituted benzyl bromides, the reciprocal of the time (in days) for 50% hydrolysis, which gives a measure of the velocity coefficient, being shown in parenthesis after each compound : *4-methoxy-α-naphthylmethyl bromide*(∞) > *4-methyl-α-naphthylmethyl bromide* (6·0) > α-naphthylmethyl bromide (0·55) > 4-bromo-α-naphthylmethyl bromide (0·29). 4-Methoxy-α-naphthylmethyl bromide resembles p-methoxybenzyl bromide in being almost instantaneously hydrolysed in aqueous alcohol, and its great reactivity, *e.g.*, in a moist atmosphere (see Experimental), must be due to the combined influences of the general and the powerful alternating effect of the methoxyl group, supplemented by a further effect due to the compound's " naphthalenoid " (as opposed to benzenoid) character. 4-Methyl-α-naphthylmethyl bromide also is very readily hydrolysed in aqueous alcohol, and the naphthalenoid enhancing influence is so great that in 2-methyl-α-naphthylmethyl bromide, in which a decreased reactivity might have been expected from steric hindrance, the bromine atom is almost as readily replaced as that in the 1 : 4-isomeride.

Whilst the hydrolysis of the methoxyl and methyl compounds proved to be too rapid to allow a satisfactory velocity coefficient to be obtained, the comparative slowness of the hydrolysis of the unsubstituted α- and β-naphthylmethyl bromides and of 4-bromo-α- and 1-bromo-β-naphthylmethyl bromides has enabled us to obtain a numerical value of the increased reactivity, due to the compounds having acquired naphthalenoid characteristics in the α or β-position, by comparing the values in Table I (k = unimolecular velocity

TABLE I.

Compound.	$k \times 10^6$.	Compound.	$k \times 10^6$.
1. $C_{10}H_7 \cdot CH_2Br(\alpha)$	270	6. $Br(4) \cdot C_{10}H_6 \cdot CH_2Br(\alpha)$ ...	137
2. $C_{10}H_7 \cdot CH_2Br(\beta)$	210	7. $Br(1) \cdot C_{10}H_6 \cdot CH_2Br(\beta)$ ...	59
3. $C_6H_5 \cdot CH_2Br$	125	8. $Br(4) \cdot C_6H_4 \cdot CH_2Br(1)$ ...	71
4. $MeO(5) \cdot C_{10}H_6 \cdot CH_2Br(\alpha)$	485	9. $Br(2) \cdot C_6H_4 \cdot CH_2Br(1)$ ...	39
5. $Br(5) \cdot C_{10}H_6 \cdot CH_2Br(\alpha)$ ...	129		

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* That formation of molecules of a quinonoid type might be intermediate in the reduction of the halogenated methylnaphthalenes appears probable in view of recent work of Schorigin (*Ber.*, 1926, **59**, 2504), who claims to have demonstrated the existence of the quinonoid modification of toluene.

coefficient at 25°). The ratio for compounds 1 and 3 is 2·16, and that for compounds 6 and 8 is 1·92; the reaction is therefore approximately twice as fast for the α-naphthalene derivatives as for the corresponding benzene derivatives. In the case of the β-naphthalene derivatives the increase is not so great, as may be seen from the ratio between Nos. 2 and 3 (1·68) and between Nos. 7 and 9 (1·52).

Definite evidence of the transmission of an influence from the 5- to the 1-position of the naphthalene nucleus has been obtained, in that the order of ease of hydrolysis of the following compounds is : 5-*methoxy*-α-*naphthylmethyl bromide* ($k = 0{\cdot}000485$) > α-naphthylmethyl bromide ($k = 0{\cdot}000270$) > 5-*bromo*-α-*naphthylmethyl bromide* ($k = 0{\cdot}000129$); it is important to note that this is the order of reactivity of the 1 : 4-isomerides, but whilst 4-methoxy-α-naphthylmethyl bromide is hydrolysed with great rapidity in aqueous-alcoholic solution, the 1 : 5-isomeride is comparatively slowly hydrolysed. This is in agreement with the generalisation of Olivier (*loc. cit.*), since α-naphthol in the form of its carbonate is brominated in the 4-position. The fact that the 5-methoxy-derivative is more reactive than the unsubstituted compound is of interest, and it is possible that in α-naphthol itself the 5-position is liable to attack, but the overwhelming reactivity of the 4-position completely masks the tendency to produce a 1 : 5-derivative.

The nuclear bromine atom in 5-bromo-α-naphthylmethyl bromide exercises a powerful retarding influence on the rate of hydrolysis of the lateral bromine atom, and the 1 : 4-isomeride ($k = 0{\cdot}000137$) is slightly but definitely more reactive than the 1 : 5-isomeride ($k = 0{\cdot}000129$), which is again in agreement with the production of more 1 : 4-dibromo- than 1 : 5-dibromo-naphthalene in the bromination of α-bromonaphthalene (Armstrong and Rossiter, *Chem. News*, 1892, **65**, 59).

The differences which exist between the hydrolysis of the 1 : 4- and 1 : 5-isomerides suggest that, whilst both alternating and general influences are readily transmitted from the 4- to the 1-position in naphthalene as in the corresponding benzene derivatives, the alternating influence does not readily pass from the 5- to the 1-position. An effect due to the general influence is apparent, *viz.*, the retarded reactivity of 5-bromo-α-naphthylmethyl bromide and the slightly enhanced reactivity of 5-methoxy-α-naphthylmethyl bromide as compared with the unsubstituted α-naphthylmethyl bromide, since bromine retards and methoxyl increases such reactivity in a general way (compare Shoesmith and Slater, J., 1926, 217).

EXPERIMENTAL.

The isomeric naphthylmethyl bromides were prepared by brominating the appropriate methylnaphthalene at the boiling point in direct sunlight. They were purified by crystallisation from alcohol; the α-isomeride had m. p. 53°, and the β- had m. p. 56°. They both possess lachrymatory properties, and produce a burning sensation on the skin.

4-*Methoxy-α-naphthylmethyl Bromide.*—4-Methoxy-α-naphthaldehyde, prepared from α-naphthyl methyl ether by Gattermann's method (*Annalen*, 1907, **357**, 365), was converted into 4-methoxy-α-naphthylcarbinol of m. p. 35° (*Anal. Fís. Quím.*, 1919, **17**, 125) by means of 66% aqueous potassium hydroxide (25% alcoholic potassium hydroxide was without action), and the carbinol, dissolved in dry benzene, was converted into the corresponding bromide by means of dry hydrogen bromide. The resulting yellow needles could not be recrystallised from any solvent owing to their great instability; they had m. p. 119—120° (decomp.) (Found: Br, hydrolysable, 24·7. $C_{12}H_{11}OBr,C_6H_6$ requires Br, 24·3%). The whole of this bromine became ionisable in 90% aqueous alcohol in 5 minutes. The yellow crystals fumed and rapidly liquefied in the atmosphere owing to hydrolysis.

An attempt to prepare 2-methoxy-α-naphthylcarbinol by a similar method was unsuccessful; 4-methoxy- and 2-methoxy-α-naphthoamides were found by Gattermann (*Annalen*, 1888, **244**, 72) to display analogous differences in their behaviour with potassium hydroxide; moreover 2-methoxy-α-naphthaldehyde gives anomalous results with Schiff's reagent. An attempt to obtain the carbinol by reduction of 2-methoxy-α-naphthaldoxime (by means of sodium amalgam in glacial acetic acid) to the corresponding amine also failed. This suggests that reactions involving the carbon atom of the aldehyde group are inhibited by the proximity of the methoxyl group on the one side and the additional ring system on the other.

An attempt was also made to prepare 3-methoxy-α-naphthylmethyl bromide, and the synthesis was carried as far as the corresponding alcohol, but insufficient of this was obtained for the purpose.

3-*Methoxy-α-naphthaldehyde.*—α-Naphthylamine-3 : 8-disulphonic acid (100 g.), dissolved in 1 l. of water containing 25 g. of sodium hydroxide, was reduced with 200 g. of 4% sodium amalgam, and the α-naphthylamine-3-sulphonic acid was converted into 3-*methoxy-α-naphthaldehyde* by the methods already given (J., 1926, 3241). Especial care was necessary to ensure the absence of 3-hydroxy-α-naphthoic acid from the intermediate 3-methoxy-α-naphthoic acid; this was converted into 3-*methoxy-α-naphthoyl chloride*, yellow needles from light petroleum, m. p. 79° (Found : Cl, 15·5. $C_{12}H_9O_2Cl$ requires Cl, 16·1%), which was catalytically reduced. The aldehyde crystallises from light petroleum in colourless, rhombic plates, m. p. 60° (Found : C, 77·1; H, 5·4. $C_{12}H_{10}O_2$ requires C, 77·5; H, 5·4%); *oxime*, white needles from aqueous alcohol, m. p. 102°; p-*nitrophenylhydrazone*, brick-red needles from acetic acid, m. p. 197°; *semicarbazone*, white needles from aqueous alcohol, m. p. 200°. The yield of aldehyde is very small and only sufficient was obtained for characterisation and conversion as above into a small sample of 3-*methoxy-α-naphthylcarbinol*. The carbinol crystallised from water in fine, colourless needles, m. p. 88° (Found : C, 76·1; H, 6·4. $C_{12}H_{12}O_2$ requires C, 76·5; H, 6·4%).

4-Bromo-α-naphthol was prepared by Reverdin and Kauffmann's method (*Ber.*, 1895, **28**, 3053) and, when purified by steam distillation in an atmosphere of nitrogen, was obtained as colourless needles, m. p. 129°. When the intermediate 4-bromo-α-naphthyl carbonate is treated in methyl-alcoholic solution alternately with 5% methyl-alcoholic potassium hydroxide and methyl sulphate in an atmosphere of nitrogen, 4-*bromo-α-naphthyl methyl ether*, a colourless oil, b. p. 181°/18 mm. (Found : Br, 33·6. $C_{11}H_9OBr$ requires Br, 33·8%), may be obtained.

1-Bromo-β-naphthol, prepared by direct bromination of β-naphthol and repeatedly crystallised from acetic acid, had m. p. 84°.

1-Bromo-β- and 4-bromo-α-methylnaphthalenes were prepared by direct bromination of β- and α-methylnaphthalene, respectively, and purified by repeated fractionation in a vacuum. The samples used in the reduction experiments were free from hydrolysable bromine. They were converted into 1-bromo-β-naphthylmethyl bromide (m. p. 107°) and 4-bromo-α-naphthylmethyl bromide (m. p. 103°), respectively, by a current of dry bromine at 210—220°, and recrystallisation from light petroleum (Mayer and Sieglitz, *Ber.*, 1922, **55**, 1839).

4-*Methyl-α-naphthylmethyl Bromide.*—4-Bromo-1-methylnaphthalene (13 g.) was treated in ethereal solution with magnesium (1·5 g.), and after the vigorous reaction had ceased paraformaldehyde (18 g.) was added, and the whole heated for 48 hours; the product was mixed with ice and sulphuric acid, extracted with ether, the ether evaporated, the residual oil dissolved in alcohol, and the 4-methyl-α-naphthylcarbinol, m. p. 75°, obtained by fractionally precipitating the oil first with water. The carbinol was converted into 4-*methyl-α-naphthylmethyl bromide* in dry benzene by means of hydrogen bromide. It crystallised from light petroleum in long needles, m. p. 77° (Found : Br, 34·3. $C_{12}H_{11}Br$ requires Br, 34·0%).

2-Methyl-α-naphthylmethyl bromide was obtained similarly from 1-bromo-2-methylnaphthalene, and had m. p. 88° (Ziegler and Tiemann, *Ber.*, 1922, **55**, 3411).

For comparative purposes, ω-bromo-*p*-xylene was prepared from *p*-toluonitrile by reduction by Stephen's method (J., 1925, **127**, 1874) to *p*-tolualdehyde, and thence by 25% alcoholic potassium hydroxide to *p*-tolylcarbinol, which gave ω-bromo-*p*-xylene on treatment with hydrogen bromide. This should also prove a more convenient method for the preparation of the meta-isomeride than any yet published.

Attempts to prepare 4-bromo-2-methylnaphthalene were without appreciable success; the method of Vesely and Kapp (*Rec. trav. chim.*, 1925, **44**, 371) failed to produce a satisfactory yield of the required 4-amino-2-methylnaphthalene, and a method involving the bromination of aceto-2-methyl-α-naphthalide with subsequent elimination of the amino-group yielded only a trace of impure 4-bromo-2-methylnaphthalene.

Aceto-4-bromo-2-methyl-α-naphthalide.—Aceto-2-methyl-1-naphthalide (Lesser, *Annalen*, 1913, **402**, 38) (5 g.) was dissolved in 25 c.c. of glacial acetic acid, and bromine (5 g.) in glacial acetic acid (3 c.c.) slowly added. After 1 hour, the mixture was poured into water; the precipitate obtained crystallised from alcohol in flocculent needles, m. p. 223° (Found: Br, 28·7. $C_{13}H_{12}ONBr$ requires Br, 28·8%). This acetyl derivative was hydrolysed by a boiling mixture of hydrochloric acid (8 parts) and alcohol (8 parts). After 6 hours, the whole was poured into water, and concentrated ammonia added to the hot solution. The precipitated 4-*bromo-2-methyl-α-naphthylamine* crystallised from light petroleum in white needles (rapidly becoming pink in the air), m. p. 82° (Found: Br, 33·4. $C_{11}H_{10}NBr$ requires Br, 33·9%); the yield was very poor.

5-*Bromo-α-naphthylmethyl Bromide.*—The bromination of α-naphthoic acid dissolved in warm glacial acetic acid produced 5-bromo-α-naphthoic acid, which, when recrystallised several times from alcohol, had m. p. 262° (Found: Br, 31·5. Calc.: Br, 31·8%) (Eckstrand, *J. pr. Chem.*, 1888, **38**, 155, gives m. p. 246°; Raiford and Lankelma, *J. Amer. Chem. Soc.*, 1925, **47**, 1119, give 244°). The acid was converted by means of thionyl chloride into 5-bromo-α-naphthoyl chloride (compare Raiford and Lankelma, *loc. cit.*); this was recrystallised from light petroleum (b. p. 40—60°), and reduced by Rosenmund's method (*Ber.*, 1918, **51**, 591) to 5-bromo-α-naphthaldehyde (see Rupe and Metzger, *Helv. Chim. Acta*, 1925, **8**, 838), which crystallised from light petroleum in white, prismatic needles, m. p. 104° (Found: Br, 33·9. Calc.: Br, 34·1%); p-*nitrophenylhydrazone*, red needles from acetic acid, m. p. 263°. The aldehyde was allowed to stand in contact with twice its weight of 66% aqueous potassium hydroxide and a few drops of alcohol for 3 days, being warmed for a few minutes each day to 60°. When reduction was considered to be complete, the reaction mixture was diluted with water and extracted with ether, the extract shaken with sodium bisulphite solution to remove unchanged aldehyde, and the ether evaporated. The *5-bromo-α-naphthylcarbinol* so obtained crystallised from light petroleum as fine, white needles, m. p. 124° (Found : C, 55·5; H, 3·7. $C_{11}H_9OBr$ requires C, 55·7; H, 3·8%). Dry hydrogen bromide passed into the benzene solution of this gave *5-bromo-α-naphthylmethyl bromide,* which crystallised from light petroleum in white needles, m. p. 101° (Found : Br, hydrolysable, 26·7. $C_{11}H_8Br_2$ requires Br, hydrolysable, 26·8%).

5-Methoxy-α-naphthylmethyl Bromide.—5-Methoxy-α-naphthaldehyde (Shoesmith and Rubli, J., 1926, 3241) was prepared in a relatively large quantity (5 g.). The purification of 5-methoxy-α-naphthoic acid was more economically effected by repeated crystallisation than by our former method, and Dr. C. E. Sosson has obtained a sample of m. p. 230°. The corresponding acid chloride, obtained by the use of thionyl chloride, yields the aldehyde on reduction (yield, 30—40%).

The aldehyde was reduced as in the case of the bromo-compound above; the *5-methoxy-α-naphthylcarbinol* obtained crystallised from water in long, colourless needles, m. p. 98° (Found : C, 76·5; H, 6·3. $C_{12}H_{12}O_2$ requires C, 76·5; H, 6·4%); with dry hydrogen bromide in benzene solution it yielded *5-methoxy-α-naphthylmethyl bromide,* which crystallised from light petroleum (b. p. 40—60°) in white, prismatic needles, m. p. 65° (Found : Br, 31·4. $C_{12}H_{11}OBr$ requires Br, 31·9%). It is more stable in the air than the 4-methoxy-derivative. Both 5-bromo- and 5-methoxy-α-naphthylmethyl bromides produce a burning sensation on the skin, but neither is lachrymatory.

5-Bromo-α-naphthol.—Bromine (40 g.) was gradually dropped into vigorously stirred, *dry,* molten α-nitronaphthalene (85 g.), the temperature being maintained at 80—100°. 5-Bromo-α-nitronaphthalene, m. p. 122°, was obtained pure by crystallising the reaction mixture from alcohol, and was reduced by West's method (J., 1925, **127**, 994) to 5-bromo-α-naphthylamine, which crystallised from ligroin in plates, m. p. 69°. The insoluble sulphate of this compound was diazotised in the usual manner. The rather stable diazonium sulphate decomposed most satisfactorily when dropped into a boiling solution of 43% sulphuric acid; 5-bromo-α-naphthol was then distilled in steam, and crystallised as white needles, m. p. 137° (Fuson, *J. Amer. Chem. Soc.*, 1924, **46**, 2779).

Hydrolysis of Compounds containing Halogen in the Side Chain.—The hydrolyses were carried out at 25° in aqueous alcohol prepared by the addition of sufficient alcohol to every 10 c.c. of water to produce a volume of 100 c.c., 10 c.c. of the reagent being used for each 0·06 (approx.) g. of compound. Aliquot portions of the mixture were at intervals run into a large excess of water and rapidly titrated with standard alkali. The resulting unimolecular velocity coefficient, k (Table I), was satisfactorily constant in each case.

The rapidity of hydrolysis of 4-methyl-α-naphthylmethyl bromide (A) and 2-methyl-α-naphthylmethyl bromide (B) is seen from Table II, in which the hydrolysis of 4-bromo-α-naphthylmethyl bromide (C) is included for comparison, and t, w, and x have the same significance as in former publications.

TABLE II.

	A.	B.		C.
w =	0·5172	0·5080		0·6125
t (hours).	x.	x.	t (days).	x.
2	29	24	2	32·4
4	50	45	3	44·8
8	68	65	4	54·7
25	95	94	7	75·1

TABLE III.

	Reagent.				
Compound.	$C_2H_4O_2$ (c.c.).	HI (c.c.).	T.	t (hrs.).	x.
$C_{10}H_7Br(\alpha)$	10	10	100°	4	4
$C_{10}H_7Br(\beta)$	,,	,,	,,	,,	Nil
$C_{10}H_7I(\alpha)$	,,	,,	,,	,,	62
$C_{10}H_7I(\beta)$	,,	,,	,,	,,	7
$C_{10}H_7{\cdot}CH_2Br(\alpha)$	,,	,,	,,	1	96
,,	,,	,,	77	2	40
,,	,,	,,	,,	4	65
$C_{10}H_7{\cdot}CH_2Br(\beta)$	,,	,,	100	1	96
,,	,,	,,	77	2	42
,,	,,	,,	,,	4	71
$Br(1){\cdot}C_{10}H_6{\cdot}OH(\beta)$	15	5	,,	0·25	94*
,,	22	,,	25	0·50	63
,,	,,	,,	,,	0·75	76
,,	,,	,,	,,	1·50	93
$Br(4){\cdot}C_{10}H_6{\cdot}OH(\alpha)$	15	,,	77	0·25	95*
,,	22	,,	25	0·50	27
,,	,,	,,	,,	0·75	38
,,	,,	,,	,,	1·50	63
$Br(1){\cdot}C_{10}H_6{\cdot}CH_3(\beta)$	10	,,	100	2	60
,,	,,	,,	,,	4	78
,,	,,	,,	,,	6	88
$Br(4){\cdot}C_{10}H_6{\cdot}CH_3(\alpha)$	,,	,,	,,	2	29
,,	,,	,,	,,	4	50
,,	,,	,,	,,	6	62
$Br(5){\cdot}C_{10}H_6{\cdot}OH(\alpha)$	,,	,,	,,	5	20

* The ease of reduction of these compounds is indicated here.

The reciprocal of the time (in days) taken for half hydrolysis of ω-bromo-*p*-xylene was 1·0.

Reduction of Various Halogenated Naphthalene Derivatives.—In Table III are summarised all the results of the reduction experiments with hydriodic acid. These were carried out in the usual manner, approximately 0·170 g. of each compound being used in glacial acetic acid and constant-boiling hydriodic acid; t and x have their usual significance, whilst T is the temperature of experiment. The liberated iodine in each case was taken as a measure of the amount of reduction which had taken place.

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