603. *The Halogenation of β-Naphthylamine and its Derivatives.*

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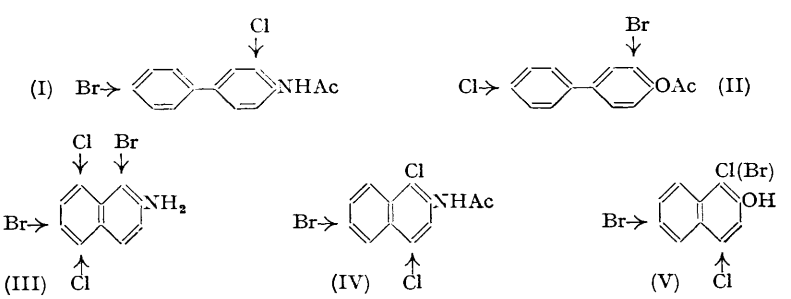
A comparison has been made between the action of chlorine and of bromine on a number of 2-sulphonamidonaphthalenes, and the properties of a number of additive compounds are described.

Modern theories of substitution tend to ignore the differences which exist between the action of chlorine and of bromine on aromatic compounds. Such differences are most clearly perceived in compounds containing more than one nucleus. Thus 4-acetamidodiphenyl (I) undergoes chlorination in position 3 but brominates mainly in position 4′ (Scarborough and Waters, *J.*, 1926, 557; Kenyon and Robinson, *J.*, 1926, 3050). On the other hand 4-acetoxydiphenyl (II) brominates in position 3 and chlorinates in position 4′, a result which indicates that mere size of the halogen atom scarcely enters into the problem (Savoy and Abernethy, *J. Amer. Chem. Soc.*, 1942, **64**, 2220, 2719). Many similar examples are found in the naphthalene series. β-Naphthylamine (III) in sulphuric acid solution chlorinates in positions 5 : 8 (Claus and Philipson, *J. pr. Chem.*, 1891, **43**, 58) but brominates in positions 1 : 6 (Claus and Jack, *J. pr. Chem.*, 1898, **57**, 1). Again, whereas 1-chloro-2-acetonaphthalide (IV) in acetic acid chlorinates in position 4 (Clemo and Legg, *J.*, 1947,

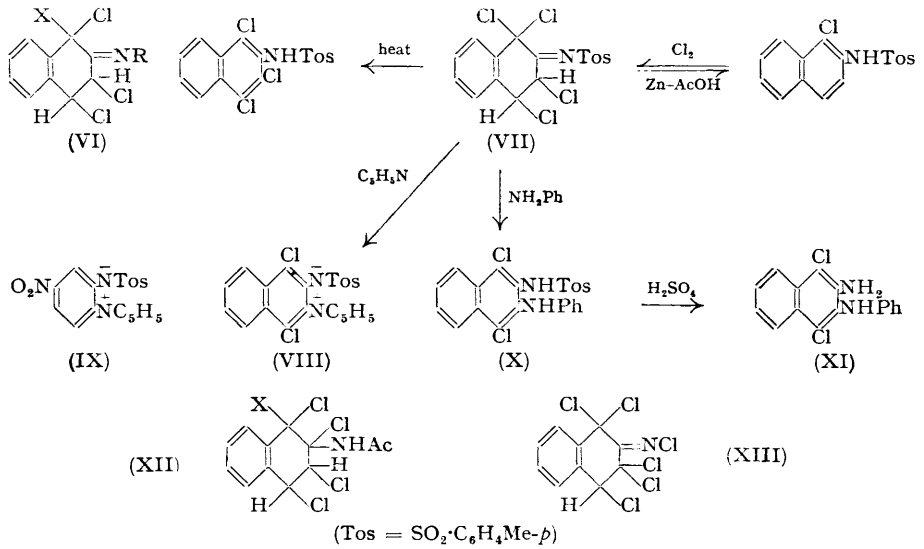


543) it brominates in position 6 (Armstrong and Rossiter, *Chem. News*, 1891, **63**, 137) and, similarly, β-naphthol (V) yields the 1 : 6-dibromo-derivative but the 1 : 4-dichloro-derivative (James and Woodcock, *J.*, 1951, 1931).

Halogenation may follow a free-radical mechanism, may involve a transition complex with positive halogen entering the nucleus, or may proceed by an addition–elimination process. The fundamental differences between chlorine and bromine which determine the relative likelihood of these routes may be modified by choice of solvent. Although the addition–elimination process of substitution is at present generally ignored or even rejected, the only positive evidence against it appears to be that in a paper by Price (*J. Amer. Chem. Soc.*, 1936, **58**, 2101) which contains a study of but one particular reaction, *viz.*, the conversion of phenanthrene into 9-bromophenanthrene. It was thought that a study of the halogenation of 2-sulphonamidonaphthalenes might throw light on these effects.

The monohalogenation of 2-toluene-*p*-sulphonamidonaphthalene to yield the 1-chloro- and 1-bromo-derivatives has already been described (Schuloff, Pollak, and Riess, *Ber.*, 1929, **62**, 1853; Bell, *J.*, 1932, 2733). The direction of further bromination of either of these compounds is determined entirely by the solvent. In acetic acid or chloroform position 6 is attacked, but in pyridine position 3. In view of the well-established normal inertness of position 3 in β-naphthylamine derivatives, this indicates that conditions are particularly favourable to bromination in pyridine solution, a point supported by the ready conversion of 2 : 4-dichlorotoluene-*p*-sulphonanilide into the 6-bromo-derivative under these conditions. It appears probable that the effectiveness of this method of bromination is, in part, due to attack by positive bromine derived from the additive compound, $C_5H_5NBr_2$ (Trowbridge and Diehl, *J. Amer. Chem. Soc.*, 1897, **19**, 567). This suggested that *N*-bromosuccinimide would be equally effective under the same conditions and such proved to be the case, 2-toluene-*p*-sulphonamidonaphthalene, for example, readily yielding the 1 : 3-dibromo-derivative.

Chlorine in pyridine solution was of no value as a chlorinating agent, probably owing to the ease with which chloropyridines are produced (Sell and Dootson, *J.*, 1898, **73**, 442; Reitzenstein and Breuning, *J. pr. Chem.*, 1911, **83**, 120). It was not possible in any example studied to convert a sulphonanilide into a chloro-derivative by means of this



(Tos = $SO_2 \cdot C_6H_4Me$-*p*)

reagent. The favourable result with *N*-bromosuccinimide suggested that *N*-chlorosuccinimide might prove equally effective, in spite of previous negative results (Ziegler, Spath, Schaaf, Schumann, and Winkelmann, *Annalen*, 1942, **551**, 80). It was found that 2-toluene-*p*-sulphonamidonaphthalene in pyridine could be converted into the 1-chloro-derivative in fair yield. Further chlorination to the 1 : 3-dichloro-derivative could not be brought about, nor could 2 : 4-dichlorotoluene-*p*-sulphonanilide be converted into

the 2 : 4 : 6-trichloro-derivative. 1-Bromo-2-toluene-*p*-sulphonamidonaphthalene, however, gave a small yield of a dichloro-derivative.

The action of chlorine on acetic acid or chloroform solutions of 1-chloro(or bromo)-2-sulphonamidonaphthalenes led to the production of stable additive compounds of type (VI; X = Cl or Br, R = SO_2Ph, $SO_2{\cdot}C_6H_4Me$, or $SO_2{\cdot}C_6H_4{\cdot}NO_2$) which do not liberate iodine from potassium iodide. Similar additive compounds were not obtained from 1 : 3-dichloro-, 1 : 3 : 4-trichloro-, 1 : 3-dibromo-, 1-iodo-, and 1-nitro-2-toluene-*p*-sulphonamidonaphthalenes; or from 4-chloro- and 2 : 4-dichloro-1-toluene-*p*-sulphonamidonaphthalenes; or from 2 : 4-dichlorotoluene-*p*-sulphonanilide and 3 : 5-dichlorotoluene-*p*-sulphon-4-toluidide.

The constitution assigned to these additive compounds is based on reactions which are set out for the compound (VII) derived from 1-chloro-2-toluene-*p*-sulphonamidonaphthalene. Thermal decomposition gave in good yield 1 : 3 : 4-trichloro-2-toluene-*p*-sulphonamidonaphthalene. Reduction with zinc dust and acetic acid gave 1-chloro-2-toluene-*p*-sulphonamidonaphthalene, with intermediate formation of an intensely coloured solution. With pyridine there was produced a yellow compound, readily soluble in acids and regarded as (VIII), analogous to (IX), obtained by interaction of picramic acid with toluene-*p*-sulphonyl chloride in pyridine (Bell, *J.*, 1931, 2344). That the pyridine residue does not displace the halogen atoms present in position 1 is shown by the conversion of compound (VI; X = Br, R = $SO_2{\cdot}C_6H_4Me$) into the corresponding 1-bromo-4-chloropyridinium compound (as VIII). The aniline residue in compound (X) is placed in position 3 for the same reason. Base (XI) is obtained irrespective of the identity of the sulphonyl group originally present. The thermal decomposition of mixed halogen compounds such as (VI; X = Br) resulted in evolution of bromine, but the reaction was complex and the solid products were not identified.

These additive compounds are somewhat akin in structure to (XII; X = Cl), obtained by passing chlorine into a cold chloroform solution of 1-chloro-2-acetonaphthalide (Claus and Philipson, *loc. cit.*) and (XIII), obtained by interaction of chlorine and a benzene suspension of β-naphthylamine hydrochloride (Durand and Huguenin A.G., D.R.-P. 400,254). Both products were, therefore, re-examined.

It was found that (XII; X = Cl) passed smoothly into 1 : 3 : 4-trichloro-2-acetonaphthalide when heated. The reactions with pyridine and aniline were vigorous, but identifiable products were not isolated. In hot acetic acid the compound suffered profound decomposition, and no crystalline material could be isolated from the solution. In an unsuccessful attempt to repeat the preparation of compound (XII; X = Br), obtained by Claus and Jack (*loc. cit.*) by the action of chlorine on a chloroform solution of 1-bromo-2-acetonaphthalide, a considerable amount (*ca.* 15%) of 1 : 4-dichloro-2-acetonaphthalide was isolated.

Compound (XIII) is surprisingly stable. It was precipitated unchanged after addition of water to an acetic anhydride solution which had been set aside for one week, and was recovered unchanged from solution in cold aniline. Pyridine brought about rapid decomposition to give yellow amorphous products. The dichloro-base obtained by reduction (D.R.-P. 420,754) was shown by conversion into 1 : 3-dichloronaphthalene to be 1 : 3-dichloro-2-naphthylamine. It may be noted that a 2-naphthylamine with halogen atoms in positions 1 and 3 reacts sluggishly with toluene-*p*-sulphonyl chloride but then gives the ditoluene-*p*-sulphonamide rather than the monosulphonamide (compare the behaviour of certain nitroamines; Bell, *J.*, 1929, 2787). With chlorine in acetic acid 1 : 3-dichloro-2-acetonaphthalide gave a poor yield of 1 : 3 : 4-trichloro-2-acetonaphthalide and, similarly, 1 : 3-dichloro-2-toluene-*p*-sulphonamidonaphthalene yielded the 1 : 3 : 4-trichloro-compound.

The following tentative suggestions are offered in regard to the halogenation of β-naphthylamine and its derivatives :

(*a*) Entry into positions 1 and 6 represents normal attack by " molecular " halogen under the influence of the directing group in position 2.

(*b*) Entry into position 3 results from attack by positive halogen or, less probably, a halogen radical.

(*c*) Entry into position 4 involves elimination of halogen halide from a previously formed additive compound.

Experimental

Bromination of 1-*Chloro*-2-*toluene*-p-*sulphonamidonaphthalene*.—(*a*) Bromine (1·5 g.) in acetic acid (3 c.c.) was added to the sulphonamidonaphthalene (3 g.) in warm acetic acid (20 c.c.). No crystallisation occurred even after overnight storage, so water was added. The resultant oil slowly solidified; repeated crystallisation from acetic acid gave 6-*bromo*-1-*chloro*-2-*toluene*-p-*sulphonamidonaphthalene* (1·2 g.) as needles, m. p. 163° (Found: C, 50·0; H, 3·2. $C_{17}H_{13}O_2NSClBr$ requires C, 49·7; H, 3·2%). This was hydrolysed by cold sulphuric acid (about 1 hr. required), and the resultant base acetylated to give 6-bromo-1-chloro-2-acetonaphthalide, m. p. 224°, alone or mixed with an authentic sample.

(*b*) Bromine (1·3 g.) in chloroform was added to the sulphonamidonaphthalene (2·6 g.) in chloroform, and the mixture set aside for 2 days. The deposit (1·3 g.) was slightly impure 6-bromo-1-chloro-2-naphthylamine hydrobromide. The filtrate on concentration gave 6-bromo-1-chloro-2-toluene-*p*-sulphonamidonaphthalene (1·0 g.).

(*c*) Bromine (1 mol.), diluted with light petroleum, was added to a cold solution of the compound in pyridine. After 3 hr. the mixture was decomposed with hydrochloric acid. The resultant oil soon solidified, and, after crystallisation from acetic acid, 3-*bromo*-1-*chloro*-2-*toluene*-p-*sulphonamidonaphthalene* formed needles, m. p. 186° (Found: C, 49·8; H, 3·3%). It was hydrolysed by cold sulphuric acid to 3-*bromo*-1-*chloro*-2-*naphthylamine*, needles, m. p. 100° (from methanol) (Found: C, 46·8; H, 2·7. $C_{10}H_7NClBr$ requires C, 46·5; H, 2·8%), and was converted by the usual nitrous acid–ethanol method to 3-bromo-1-chloronaphthalene, needles, m. p. 60°, from methanol–acetone (Hodgson and Hathway, *J.*, 1944, 538, give m. p. 60°). By interaction with acetic anhydride this base gave 3-*bromo*-1-*chloro*-2-*acetonaphthalide*, prisms, m. p. 204—206°, from acetic acid (Found: C, 48·2; H, 3·0. $C_{12}H_9ONClBr$ requires C, 48·2; H, 3·1%).

Bromination of 1-*Bromo*-2-*toluene*-p-*sulphonamidonaphthalene*.—(*a*) Addition of bromine (1 mol.) to the compound, m. p. 108°, in acetic acid gave a solution which was kept overnight and then diluted with water. The pasty product, after several recrystallisations from ethanol, furnished 1 : 6-dibromo-2-toluene-*p*-sulphonamidonaphthalene in poor yield.

(*b*) Bromine (1·1 g.) was added to the monobromo-compound (2·6 g.) in a small quantity of chloroform. After 2 days, 1 : 6-dibromo-2-naphthylamine hydrobromide (1·3 g.) was filtered off, and the filtrate diluted with light petroleum to give 1 : 6-dibromo-2-toluene-*p*-sulphonamidonaphthalene (1·2 g.).

2-*Bromo*-4 : 6-*dichlorotoluene*-p-*sulphonanilide*.—Bromination of 2 : 4-dichlorotoluene-*p*-sulphonanilide in pyridine solution readily gave the *bromodichloro*-compound, which formed needles, m. p. 160°, from acetic acid (Found: C, 39·8; H, 2·6. $C_{13}H_{10}O_2NSCl_2Br$ requires C, 39·5; H, 2·5%).

Experiments with N-*Bromosuccinimide*.—(*a*) 1-Chloro-2-acetonaphthalide was unchanged after being boiled in carbon tetrachloride with the reagent for 6 hr.

(*b*) Addition of the reagent to a boiling solution of 2-benzenesulphonamido-1-chloronaphthalene in carbon tetrachloride soon led to liberation of bromine. After 5 hr.' heating a brown sticky mass was obtained which was not examined further.

(*c*) Addition of the reagent (2 mol.) to 2-toluene-*p*-sulphonamidonaphthalene in pyridine, decomposition of the mixture with hydrochloric acid, and recrystallisation of the precipitate from acetic acid gave the 1 : 3-dibromo-derivative, m. p. 159°, in good yield.

(*d*) 2 : 4-Dichlorotoluene-*p*-sulphonanilide with the reagent (1 mol.) as in (*c*) gave an almost quantitative yield of the 6-bromo-derivative.

(*e*) 1-Nitro-2-toluene-*p*-sulphonamidonaphthalene with the reagent (1 mol.) as in (*c*) gave an almost quantitative yield of the 3-bromo-derivative, which crystallised from *o*-dichlorobenzene in rosettes, m. p. 237° (Consden and Kenyon, *J.*, 1935, 1593, give m. p. 237—239°).

(*f*) β-Naphthylamine, in pyridine, reacted briskly with the reagent (2 mol.). The product on decomposition with hydrochloric acid, gave a small amount of a yellow solid and an uncrystallisable black oil.

Experiments with N-*Chlorosuccinimide*.—(*a*) On addition of the reagent (1 mol.) to 1-chloro-2-toluene-*p*-sulphonamidonaphthalene in pyridine heat was evolved and the mixture became very dark. On decomposition with hydrochloric acid a plastic mass was precipitated and the solution

contained a pyridinium salt, which could be precipitated by addition of ammonium hydroxide. The plastic mass gave the original compound as the only isolable solid.

(*b*) 2 : 4-Dichlorotoluene-*p*-sulphonanilide treated as in (*a*) was recovered unchanged.

(*c*) 2-Toluene-*p*-sulphonamidonaphthalene treated as in (*a*) gave the 1-chloro-derivative, m. p. 130—131°.

(*d*) 2-Benzenesulphonamido-1-bromonaphthalene behaved as in (*a*) but the sticky mass, after repeated crystallisation from acetic acid, gave a *2-benzenesulphonamido-1-bromo-dichloronaphthalene* as prisms, m. p. 198° (Found : C, 45·3, 45·4; H, 2·6, 2·4. $C_{16}H_{10}O_2NSCl_2Br$ requires C, 44·5; H, 2·3%). *2-Benzenesulphonamido-1-bromonaphthalene* was obtained (*a*) from 1-bromo-2-naphthylamine or (*b*) by the addition of bromine (1 mol.) to 2-benzenesulphonamidonaphthalene in chloroform; the mixture was filtered from a small precipitate of hydrobromide, and the filtrate diluted with light petroleum. The bromo-compound crystallised from ethanol or acetic acid in needles, m. p. 135° (Found : N, 3·7. $C_{16}H_{12}O_2NSBr$ requires N, 3·9%).

Chlorine Addition Compounds of Type (VI).—These compounds were prepared by passing a slight excess of chlorine into a warm acetic acid or chloroform solution of the sulphonamidonaphthalene. The additive compound crystallised from the solution in acetic acid or on addition of light petroleum to the chloroform solution, and was purified by crystallisation from acetic acid, benzene, or chloroform. The following compounds were thus obtained : 1 : 1 : 3 : 4-*tetrachloro*-1 : 2 : 3 : 4-*tetrahydro*-2-*toluene*-p-*sulphonimidonaphthalene* (VII), needles, m. p. 164° (Found : C, 46·6; H, 3·1; Cl, 33·5. $C_{17}H_{13}O_2NSCl_4$ requires C, 46·7; H, 3·0; Cl, 32·5%); 1-*bromo*-1 : 3 : 4-*trichloro*-1 : 2 : 3 : 4-*tetrahydro*-2-*toluene*-p-*sulphonimidonaphthalene* (VI; X = Br, R = $SO_2{\cdot}C_6H_4Me$), mass of fine needles, m. p. 179° (decomp.) (Found : C, 42·8; H, 2·8. $C_{17}H_{13}O_2NSCl_3Br$ requires C, 42·3; H, 2·7%); 2-*benzenesulphonimido*-1 : 1 : 3 : 4-*tetrachloro*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, prisms, m. p. 143° (Found : C, 45·8; H, 2·7. $C_{16}H_{11}O_2NCl_4S$ requires C, 45·4; H, 2·6%); and 1 : 1 : 3 : 4-*tetrachloro*-1 : 2 : 3 : 4-*tetrahydro*-2-m-*nitrobenzenesulphonimidonaphthalene*, prisms, m. p. 192° (Found : C, 41·0; H, 2·2. $C_{16}H_{10}O_4N_2Cl_4S$ requires C, 41·0; H, 2·1%). A small amount of 1 : 3 : 4-*trichloro*-2-m-*nitrobenzenesulphonamidonaphthalene* was formed as a by-product in this experiment; it crystallised from a large quantity of boiling acetic acid in prisms, m. p. 226° (Found : S, 7·3. $C_{16}H_9O_4N_2Cl_3S$ requires S, 7·4%). 1 : 3 : 4-Trichloro-2-naphthylamine was recovered unchanged from its pyridine solution with *m*-nitrobenzenesulphonyl chloride. 1-*Chloro*-2-m-*nitrobenzenesulphonamidonaphthalene*, prepared either from 1-chloro-2-naphthylamine or by chlorination of 2-*m*-nitrobenzenesulphonamidonaphthalene in hot acetic acid solution, crystallised from acetic acid in prisms, m. p. 135° (Found : C, 52·8; H, 3·1. $C_{16}H_{11}O_4N_2ClS$ requires C, 52·9; H, 3·0%).

Reactions of the Addition Compounds.—(a) *Heat.* A small amount of the addition compound was kept at about 10° above its m. p. until evolution of hydrogen chloride ceased (about ¼ hr.). The dark residue when crystallised from acetic acid gave an almost quantitative yield of the corresponding 1 : 3 : 4-trichloro-2-sulphonamidonaphthalene.

The addition compounds containing bromine in position 1 under these conditions evolved bromine. The residues yielded small amounts of crystalline solids which were not identified.

(b) *Zinc dust–acetic acid.* Addition of zinc dust to a warm solution of the addition compound in acetic acid resulted in vigorous reaction and the production of a deep damson or permanganate colour which was completely discharged on addition of excess of zinc dust. The hot solution was filtered and slightly diluted whereupon the 1-chloro-2-sulphonamidonaphthalene crystallised.

1-Bromo-1 : 3 : 4-trichloro-1 : 2 : 3 : 4-tetrahydro-2-toluene-*p*-sulphonimidonaphthalene gave material, m. p. 108—109° (after one crystallisation from benzene–light petroleum), corresponding to almost pure 1-chloro-2-toluene-*p*-sulphonamidonaphthalene (large depression in m. p. on admixture with 1-bromo-2-toluene-*p*-sulphonamidonaphthalene).

(c) *Pyridine.* On addition of 1-bromo-1 : 3 : 4-trichloro-1 : 2 : 3 : 4-tetrahydro-2-toluene-*p*-sulphonimidonaphthalene to cold pyridine there was considerable heat evolution. Excess of hydrochloric acid was added, the mixture filtered, and the filtrate neutralised with ammonia solution. *Anhydro*-N-(4-*bromo*-1-*chloro*-3-*toluene*-p-*sulphonamido*-2-*naphthyl*)*pyridinium hydroxide* separated as pale yellow crystals, m. p. 266° (decomp.) after reprecipitation from dilute acetic acid by ammonia solution (Found : C, 54·6, 54·3; H, 3·9, 3·8; S, 6·6. $C_{22}H_{18}O_2N_2SClBr$ requires C, 54·0; H, 3·7; S, 6·5%).

Addition of hydrochloric acid to the deep yellow pyridine solution of 1 : 1 : 3 : 4-tetrachloro-1 : 2 : 3 : 4-tetrahydro-2-toluene-*p*-sulphonimidonaphthalene gave a small precipitate, m. p. *ca.* 190°, and a filtrate from which ammonia solution precipitated yellow crystals of *anhydro*-N-(1 : 4-*dichloro*-3-*toluene*-p-*sulphonamido*-2-*naphthyl*)*pyridinium hydroxide* (VIII), m. p. 274°

(decomp.) after reprecipitation from solution in dilute acetic acid (Found: C, 58·7; H, 3·9; Cl, 15·2; S, 7·2. $C_{22}H_{18}O_2N_2SCl_2$ requires C, 59·3; H, 4·0; Cl, 15·9; S, 7·2%). The material, m. p. *ca.* 190°, after repeated crystallisation from acetic acid gave 1 : 3 : 4-*trichloro*-2-*toluene*-p-*sulphonamidonaphthalene* as prisms, m. p. 212° (Found: Cl, 26·0. $C_{17}H_{12}O_2NSCl_3$ requires Cl, 26·6%).

(d) *Aniline.* 1 : 1 : 3 : 4-Tetrachloro-1 : 2 : 3 : 4-tetrahydro-2-toluene-*p*-sulphonimidonaphthalene reacted vigorously with cold aniline to give a clear solution which soon became semi-solid. Decomposition with dilute hydrochloric acid gave 3-*anilino*-1 : 4-*dichloro*-2-*toluene*-p-*sulphonamidonaphthalene* (X) (Found: C, 60·3; H, 4·0. $C_{23}H_{18}O_2N_2Cl_2S$ requires C, 60·4; H, 3·9%), which formed needles, m. p. 201° after repeated recrystallisation from acetic acid or benzene–light petroleum to free it from deep-violet impurities, and was hydrolysed by cold sulphuric acid to 2-*amino*-3-*anilino*-1 : 4-*dichloronaphthalene* (XI) (Found: C, 63·2; H, 4·0. $C_{16}H_{12}N_2Cl_2$ requires C, 63·4; H, 4·0%). The latter crystallised from ethanol or benzene in needles, m. p. 167°, and was recovered unchanged after being boiled with acetic anhydride; it sublimed unchanged from a strongly heated mixture with litharge.

In the same way 1-bromo-1 : 3 : 4-trichloro-1 : 2 : 3 : 4-tetrahydro-2-toluene-*p*-sulphonimidonaphthalene gave 3-*anilino*-1-*bromo*-4-*chloro*-2-*toluene*-p-*sulphonamidonaphthalene*, needles, m. p. 210°, from acetic acid (Found: N, 5·3; S, 5·9. $C_{23}H_{18}O_2N_2ClBrS$ requires N, 5·6; S, 6·4%), and 2-*amino*-3-*anilino*-1-*bromo*-4-*chloronaphthalene*, needles, m. p. 164° (decomp.), from benzene (Found: N, 8·2. $C_{16}H_{12}N_2ClBr$ requires N, 8·0%).

1 : 1 : 3 : 4-Tetrachloro-1 : 2 : 3 : 4-tetrahydro-2-*m*-nitrobenzenesulphonimidonaphthalene gave 3-*anilino*-1 : 4-*dichloro*-2-m-*nitrobenzenesulphonamidonaphthalene*, rosettes, m. p. 168° (from acetic acid) (Found: C, 53·5; H, 3·2. $C_{22}H_{15}O_4N_3Cl_2S$ requires C, 54·1; H, 3·1%). This compound was recovered after 8 hr. in cold concentrated sulphuric acid or after being boiled with ethanolic hydrogen chloride.

2-Benzenesulphonimido-1 : 1 : 3 : 4-tetrachloro-1 : 2 : 3 : 4-tetrahydronaphthalene gave 3-*anilino*-2-*benzenesulphonamido*-1 : 4-*dichloronaphthalene*, needles, m. p. 204° (from acetic acid) (Found: C, 60·2; H, 3·8. $C_{22}H_{16}O_2N_2Cl_2S$ requires C, 59·6; H, 3·6%). Hydrolysis of this by cold sulphuric acid gave material, m. p. 158—160°, which was separated by crystallisation from benzene into a small amount of a sparingly soluble compound, m. p. 230° (unidentified), and rosettes of 2-amino-3-anilino-1 : 4-dichloronaphthalene.

Experiments with 1-*Halogenated*-2-*acetonaphthalides.*—(*a*) 1 : 1 : 2 : 3 : 4-Pentachloro-1 : 2 : 3 : 4-tetrahydro-2-acetonaphthalide (XII; X = Cl) was heated at 160° for a few minutes and the product then crystallised from acetic acid giving 1 : 3 : 4-trichloro-2-acetonaphthalide.

(*b*) By passage of chlorine into a cold chloroform solution of 1-bromo-2-acetonaphthalide (6 g.) there were obtained a precipitate (1·2 g.) of the hydrochloride, m. p. 140° (decomp.), and a filtrate from which light petroleum precipitated first gummy material and then a solid (*ca.* 1 g.), m. p. 160—170°. This after repeated recrystallisation from ethanol gave pure 1 : 4-dichloro-2-acetonaphthalide, m. p. 217° alone or mixed with an authentic sample.

(*c*) 1-Bromo-2-acetonaphthalide hydrochloride was maintained at 150° until the vigorous decomposition was complete. The dark product was essentially 1-bromo-2-acetonaphthalide (Found: loss, 11·2. $C_{12}H_{10}ONBr,HCl$ requires loss, 12·1%). It may be noted that if the hydrochloride were structurally 1-bromo-1-chloro-1 : 2-dihydro-2-acetonaphthalide decomposition to give 1-chloro-2-acetonaphthalide, with a loss in weight of 27%, would be possible.

1 : 1 : 3 : 3 : 5-*Pentachloro*-2-*chloroimino*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (XIII) was prepared by the method of Durand and Huguenin A.G. (*loc. cit.*) but a clear solution was not obtained at the end of the chlorination process. The insoluble material, of high decomposition point, was filtered off and decomposed with ammonia solution. It gave a sticky product which was boiled with ethanol and filtered whilst hot. The insoluble residue formed yellow needles, m. p. 285° (from *o*-dichlorobenzene), and appeared to be 1 : 2-5 : 6-dibenzophenazine. The alcoholic filtrate gave crude 1-chloro-2-naphthylamine, best purified as the acetyl derivative, m. p. 146°.

The pentachloro-compound was precipitated unchanged by addition of water to a solution in acetic anhydride, which had been kept for 1 week. It was also recovered from solution in cold aniline but was rapidly decomposed by pyridine to give yellow amorphous products.

Reduction (D.R.-P. 420,754) of the pentachloro-compound (24 g.) gave dichloro-2-naphthylamine (10 g.) and a mixture (10 g.) of chloronaphthols, apparently mainly 1 : 3-dichloro-2-naphthol (acetyl derivative, needles, m. p. 74—76°). The base was shown to be 1 : 3-dichloro-2-naphthylamine by smooth deamination to 1 : 3-dichloronaphthalene, needles, m. p. 61° (from ethanol) (Cleve, *Ber.*, 1887, **20**, 449, gives m. p. 61°; 1 : 2-dichloronaphthalene has m. p. 35°).

1 : 3-Dichloro-2-naphthylamine could be crystallised unchanged from acetic anhydride but

with acetic anhydride containing a drop of sulphuric acid gave 1 : 3-*dichloro*-2-*acetonaphthalide*, prisms, m. p. 198—200° (from acetic acid) (Found : C, 56·6; H, 3·5. $C_{12}H_9ONCl_2$ requires C, 56·7; H, 3·5%). With toluene-*p*-sulphonyl chloride (1 mol.) in pyridine the base gave a difficultly separable mixture; with 2 mol. it gave 1 : 3-*dichloro*-2-*di*(*toluene*-p-*sulphonyl*)*amino-naphthalene*, prisms, m. p. 216° (from acetic acid) (Found : S, 12·3. $C_{24}H_{19}O_4NCl_2S_2$ requires S, 12·2%). This was smoothly hydrolysed by warm piperidine to give 1 : 3-*dichloro*-2-*toluene*-p-*sulphonamidonaphthalene*, needles, m. p. 185°, from acetic acid (Found : S, 8·75. $C_{17}H_{13}O_2NSCl_2$ requires S, 8·75%).

1 : 3 : 4-*Trichloro*-2-*di*(*toluene*-p-*sulphonyl*)*aminonaphthalene*, obtained by interaction of 1 : 3 : 4-trichloro-2-naphthylamine with toluene-*p*-sulphonyl chloride (2 mols.) in pyridine, crystallised from acetic acid in prisms, m. p. 248° (Found : S, 11·7. $C_{24}H_{18}O_4NCl_3S_2$ requires S, 11·5%). It was converted into the monotoluenesulphonamide by dissolution in warm piperidine.

Miscellaneous Chlorinations.—(*a*) By passage of chlorine into a solution of 1 : 3-dichloro-2-toluene-*p*-sulphonamidonaphthalene there was obtained 1 : 3 : 4-trichloro-2-toluene-*p*-sulphonamidonaphthalene, unchanged after further treatment in acetic acid solution with chlorine.

(*b*) Chlorine was passed into a hot solution of 1 : 3-dichloro-2-acetonaphthalide in chloroform, the solvent chloroform was evaporated, and the residue was boiled with benzene; about half of the starting material was recovered and the product was an uncrystallisable gum. This experiment was repeated with acetic acid as solvent; a small yield of 1 : 3 : 4-trichloro-2-acetonaphthalide was obtained but most of the compound had been converted into a pale yellow, uncrystallisable gum.

(*c*) Passage of chlorine into a cold chloroform solution of 1-iodo-2-toluene-*p*-sulphonamidonaphthalene (Consden and Kenyon, *J.*, 1935, 1591) led to rapid liberation of iodine, and no crystalline product could be obtained.

(*d*) No identified product could be isolated from the reaction of 1-nitro-2-toluene-*p*-sulphonamidonaphthalene with chlorine in either chloroform or acetic acid.

(*e*) Chlorination of 1-toluene-*p*-sulphonamidonaphthalene in either acetic acid or chloroform led to the 4-chloro- and then the 2 : 4-dichloro-derivative (m. p. 192°), but there was then no further reaction.

(*f*) 2 : 4-Dichlorotoluene-*p*-sulphonanilde was recovered after treatment with chlorine in acetic acid solution.

(*g*) 1-*Chloro*-2-*toluene*-p-*sulphonmethylamidonaphthalene*, prepared (i) by the methylation of 1-chloro-2-toluene-*p*-sulphonamidonaphthalene and (ii) by the chlorination of 2-toluene-*p*-sulphonmethylamidonaphthalene in acetic acid solution, crystallised from acetic acid or benzene–light petroleum in needles, m. p. 123—124° (Found : C, 62·6; H, 4·7. $C_{18}H_{16}O_2NClS$ requires C, 62·5; H, 4·6%). On chlorination in chloroform solution this compound gave an uncrystallisable resin.

(*h*) 1 : 4-*Dichloro*-2-*toluene*-p-*sulphonamidonaphthalene*, prepared by interaction of 1 : 4-dichloro-2-naphthylamine (Clemo and Legg, *J.*, 1947, 543) and toluene-*p*-sulphonyl chloride in pyridine, crystallised from acetic acid in needles, m. p. 144° (Found : C, 55·7; H, 3·6. $C_{17}H_{13}O_2NSCl_2$ requires C, 55·7; H, 3·6%). Passage of chlorine into a solution of this compound gave a very small amount of a compound, which formed prisms, m. p. 230°, from acetic acid, and appeared to be an isomer of the starting material (Found : C, 55·5; H, 3·7%).

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