The Interaction of 2-Benzenesulphonamido-1-bromonaphthalene with Chlorine.

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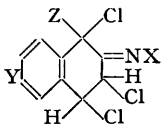
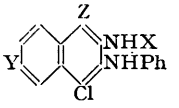
Chlorination of 2-benzenesulphonamido-1-bromonaphthalene follows a complex course but the structure of the only purely aromatic compound obtained, namely, 2-benzenesulphonamido-1 : 4-dichloronaphthalene, is most readily accounted for by an addition-elimination mechanism.

Recently it was shown (Bell, *J.*, 1953, 3035) that sulphonyl derivatives of β-naphthylamine with excess of chlorine normally yield compounds of type (I) and that these are decomposed by aniline to yield anilino-derivatives, probably of formula (II) and by pyridine to yield pyridinium salts, probably of type (III). It is now found that chlorination of 2-benzenesulphonamido-1-bromonaphthalene shows many exceptional features. At least five compounds are produced, and usually all are present in the reaction product. Three of these are readily identified, namely, 2-benzenesulphonamido-1 : 4-dichloro-, -1-bromo-1 : 3 : 4-trichloro-, and 1 : 1 : 3 : 4-tetrachloro-1 : 2 : 3 : 4-tetrahydronaphthalene (I; Z = Br or Cl, X = SO_2·Ph; Y = H). A fourth may have structure (IV) since Fries and Schimmelschmidt (*Annalen*, 1930, **484**, 287) have obtained an analogous bromine compound from β-naphthol; this product is stable towards concentrated hydrochloric acid at 100° but can be reduced by zinc and acetic acid to 2-benzenesulphonamido-1-chloronaphthalene and is decomposed above the m. p. to give, amongst other products, 2-benzenesulphonamido-1 : 4-dichloronaphthalene. With aniline it gives a compound, easily reduced to 2-benzenesulphonamido-1-chloronaphthalene; structure (V) is provisionally


(I)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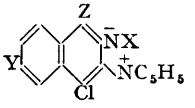
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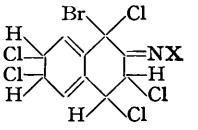
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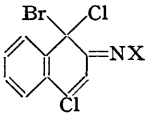
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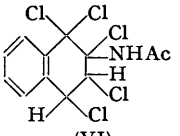
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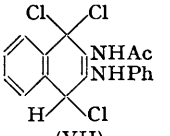
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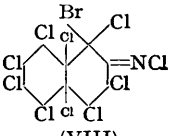
(VIII)

(Z = Cl or Br; X = SO_2·R; Y = H, Cl, or Br)

assigned to it; with pyridine it yields a compound stable either to reduction or to the action of concentrated sulphuric acid. The fifth compound, isomeric with (IV) and also stable to warm hydrochloric acid, gave with aniline a typical anilino-derivative (II; Z = Br, X = SO_2·Ph), hydrolysable to 3-anilino-1-bromo-4-chloro-2-naphthylamine, and with pyridine gave 2-benzenesulphonamido-1 : 4-dichloronaphthalene in small yield together with gummy pyridinium salts.

The surprising nature of some of the above decomposition products suggested an examination of (*a*) the thermal decomposition of 1-bromo-1 : 3 : 4-trichloro-2-toluene-*p*-sulphonimido-1 : 2 : 3 : 4-tetrahydronaphthalene (I; Y = H, Z = Br, X = SO_2·C_7H_7) and (*b*) the interaction of compound (VI) (Claus and Philipson, *J. prakt. Chem.*, 1891, **43**, 58) with aniline. In the first reaction bromine and halogen acid were evolved and a mixture of compounds obtained from which only one, regarded as (V; X = SO_2·C_7H_7), could be isolated in a pure condition. This was reduced by zinc dust and acetic acid to 1 : 4-dichloro-2-toluene-*p*-sulphonamidonaphthalene. In the second reaction a compound was produced which lacked the stability of the normal anilino-compounds in so far as it evolved hydrogen chloride above its m. p. It is regarded as (VII).

It is noteworthy that 1 : 1 : 3 : 4-tetrachloro-1 : 2 : 3 : 4-tetrahydro-2-toluene-*p*-sulphonimidonaphthalene (I; Y = H, Z = Cl, X = $SO_2 \cdot C_7H_7$) will not add additional amounts of either chlorine or bromine and, further, that 2-benzenesulphonamido-1 : 6-dibromo- and -1 : 6-dichloro-naphthalene yield chlorine compounds of type (I) (X = SO_2·Ph, Z = Br or Cl, Y = Br or Cl) without complicating side products.

1-Bromo-2-naphthylamine when treated with chlorine under the general conditions outlined in D.R.-P. 400,254 (Durand and Huguenin A.G.) gave compounds of high halogen content, one of which may be a derivative of decalin (VIII).

Experimental

2 : 4-Dichlorobenzenesulphonanilide was unchanged after dissolution in warm sulphuryl chloride; this shows that chlorine is unlikely to enter the $-SO_2$·Ph residue in any of the subsequent experiments.

1 : 1 : 3 : 4-Tetrachloro-1 : 2 : 3 : 4-tetrahydro-2-toluene-*p*-sulphonimidonaphthalene was unchanged after boiling in acetic acid with bromine or after passage of chlorine into a solution in chloroform.

2-*Benzenesulphonimido*-6-*bromo*-1 : 1 : 3 : 4-*tetrachloro*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, obtained in the usual way from 2-benzenesulphonamido-6-bromo-1-chloronaphthalene, formed prisms, m. p. 186° (Found: C, 38·3; H, 1·9. $C_{16}H_{10}O_2NBrCl_4S$ requires C, 38·3; H, 2·0%).

2-*Benzenesulphonimido*-1 : 1 : 3 : 4 : 6-*pentachloro*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, prepared from 2-benzenesulphonamido-6-chloronaphthalene, formed needles, m. p. 178—180° (Found: Cl, 38·9. $C_{16}H_{10}O_2NCl_5S$ requires Cl, 38·8%). The authors are indebted to Mr. D. P. Veitch, B.Sc., for this description.

2-*Benzenesulphonamido*-1 : 6-*dibromonaphthalene*, from 1 : 6-dibromo-2-naphthylamine and benzenesulphonyl chloride in pyridine or, in rather poor yield, by the bromination of 2-benzenesulphonamido-1-bromonaphthalene in chloroform, crystallised from acetic acid in needles, m. p. 169° (Found: C, 43·8; H, 2·8. $C_{16}H_{11}O_2NBr_2S$ requires C, 43·5; H, 2·5%). By passage of chlorine (3 mols.) into a chloroform solution of the dibromo-compound and subsequent concentration there was obtained 2-*benzenesulphonimido*-1 : 6-*dibromo*-1 : 3 : 4-*trichloro*-1 : 2 : 3 4-*tetrahydronaphthalene* as a snow-white crystalline powder, m. p. 195°, after recrystallisation from chloroform (Found: C, 35·4; H, 1·9. $C_{16}H_{10}O_2NBr_2Cl_3S$ requires C, 35·1; H, 1·8%). Although it separates from boiling acetic acid in a highly crystalline state the m. p. is less sharp. This additive compound reacted readily with aniline to give 3-*anilino*-2-*benzenesulphonimido*-1 : 6-*dibromo*-4-*chloronaphthalene*, which crystallised from acetic acid in needles, m. p. 196° (Found: C, 46·9; H, 2·6. $C_{22}H_{15}O_2N_2Br_2ClS$ requires C, 46·6; H, 2·6%), and with pyridine to give a typical *anhydro-pyridinium* derivative, which formed a yellow powder, m. p. 280° (Found: C, 45·1; H, 2·6. $C_{21}H_{13}O_2N_2SClBr_2$ requires C, 45·6; H, 2·4%).

By addition of zinc dust to a solution of the trichloro-compound in boiling acetic acid until the first developed intense colour was completely discharged there was produced 2-*benzenesulphonamido*-6-*bromo*-1-*chloronaphthalene*, which crystallised from acetic acid in needles, m. p. 153° (Found: C, 47·6; H, 3·1. $C_{16}H_{11}O_2NSClBr$ requires C, 48·4; H, 2·8%).

The trichloro-compound evolved bromine at 200° and in a short time resolidified. More soluble material was extracted by acetic acid, and the residue boiled with *o*-dichlorobenzene and filtered hot. The bright yellow residue had m. p. >310° and was appreciably volatile; the crystalline crop had m. p. 210—212°, but was visibly contaminated by the less soluble compound. It was not examined further.

1 : 3 : 4-*Trichloro*-2-*di*(*benzenesulphonyl*)*aminonaphthalene*, obtained by interaction of 1 : 3 : 4-trichloro-2-naphthylamine with benzenesulphonyl chloride (2 mols.) in pyridine, crystallised from acetic acid in needles, m. p. 262° (Found: S, 12·6. $C_{22}H_{14}O_4NS_2Cl_3$ requires S, 12·2%). By dissolution in piperidine it gave 2-*benzenesulphonamido*-1 : 3 : 4-*trichloronaphthalene*, which formed needles, m. p. 213°, from acetic acid (Found: S, 7·8. $C_{16}H_{10}O_2NSCl_3$ requires S, 8·3%).

Interaction of 2-*Benzenesulphonamido*-1-*bromonaphthalene with Chlorine*.—The undermentioned compounds were obtained in the ways outlined. Normally all are present in the reaction product and the separation is tedious and yields of purified products low.

(a) *Compound A*, m. p. 195° (decomp.) [Found: C, 35·3, 35·7; H, 1·9, 2·4. $C_{16}H_{11}O_2NSCl_5Br$ (IV) requires C, 35·65; H, 2·0%]. (i) By passage of chlorine (3·5 mols.) into the sulphonamide in cold chloroform. It constituted the least soluble product and recrystallised from a large volume of chloroform or from acetic acid (yield, *ca.* 2 g. from 10 g. of the sulphonamide). (ii) By

dissolution of the sulphonamide in sulphuryl chloride. The sticky residue remaining after evaporation of the excess of sulphuryl chloride was purified by repeated recrystallisation from acetic acid.

(b) *Compound B*, m. p. 187° (decomp.) (Found: C, 36·1; H, 2·0%). (i) As under (i) above, but with a rather smaller proportion of chlorine. It may be separated from compound A by reason of its greater solubility in chloroform. Use of alumina results in decomposition of the compounds. (ii) By interaction of the sulphonamide in chloroform with sulphuryl chloride (3 mols.).

(c) *Compound C*, m. p. 161° (decomp. 165°). Obtained on one occasion only in very small yield in process (b ii) as the least soluble compound. It crystallised from acetic acid in colourless prisms and, owing to the small quantity available, was not examined further.

2-*Benzenesulphonimido*-1-*bromo*-1 : 3 : 4-*trichloro*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m. p. 158° (Found: C, 41·0; H, 2·3. $C_{16}H_{11}O_2NCl_3BrS$ requires C, 41·1; H, 2·3%). As under (a i) and separated from A by its higher solubility in chloroform. It was purified by recrystallisation from acetic acid and gave the usual anhydropyridinium compound with pyridine.

2-Benzenesulphonimido-1 : 1 : 3 : 4-tetrachloro-1 : 2 : 3 : 4-tetrahydronaphthalene, m. p. 145° (*J.*, 1953, 3037), was the most soluble compound produced in both methods (a i and ii) and was alternatively prepared by dissolution of 2-benzenesulphonamidonaphthalene in sulphuryl chloride. It reacted with pyridine to give an anhydropyridinium compound.

2-*Benzenesulphonamido*-1 : 4-*dichloronaphthalene*, m. p. 178° (Found: C, 54·9; H, 3·0. $C_{16}H_{11}O_2NSCl_2$ requires C, 54·6; H, 3·1%). (i) As under (b ii). (ii) From 1 : 4-dichloro-2-naphthylamine (Clemo and Legg, *J.*, 1947, 543). It crystallised from acetic acid in stout needles. The material obtained in process (i) was sometimes difficult to purify and on occasions, although highly crystalline, had a m. p. *ca.* 168° and a lower carbon content (*e.g.*, C, 51·6; H, 2·8%). This behaviour is attributed to the presence of 2-benzenesulphonamido-1-bromo-4-chloronaphthalene (Calc. for $C_{16}H_{11}O_2NSClBr$: C, 48·4; H, 2·8%) although this was not obtained pure.

Reactions of Compound A (IV ?).—(i) On addition of excess of zinc dust to a suspension of A in boiling acetic acid a clear solution was rapidly obtained, which on slight dilution deposited 2-benzenesulphonamido-1-chloronaphthalene in needles, m. p. 131°. There is negligible depression in m. p. on admixture of 2-benzenesulphonamido-1-chloro- and -1-bromo-naphthalene (and similarly with other related pairs in this series). Use was made of the fluorescein test to distinguish between them. (ii) Aniline was added to compound A. Heat was evolved and a clear solution obtained which almost immediately set to a paste. After a few minutes the excess of aniline was removed by dilute hydrochloric acid. The residual plastic mass solidified under boiling acetic acid, and the product on crystallisation from ethanol gave prisms, m. p. 99—101° (Found: C, 44·4; H, 3·2%), which, dissolved in acetic acid, were converted by addition of zinc dust into 2-benzenesulphonamido-1-chloronaphthalene. This compound may be 2-*benzenesulphonimido*-1-*bromo*-1 : 4-*dichloro*-1 : 2-*dihydronaphthalene* (V; X = SO_2·Ph) ($C_{16}H_{10}O_2NSCl_2Br$ requires C, 44·6; H, 2·3%). (iii) Pyridine reacted briskly with compound A to give a yellow solution. This was decomposed by dilute hydrochloric acid and filtered. The filtrate on addition of ammonia solution yielded a sticky, yellow pyridinium compound, which was not obtained pure. The part insoluble in hydrochloric acid readily crystallised from chloroform in prisms, m. p. 233° (Found: C, 42·2, 42·3; H, 2·1, 2·5; S, 6·8%). This compound was unchanged when kept overnight with concentrated sulphuric acid or boiled in acetic acid with zinc dust. (iv) Compound A was heated above the m. p. for a short time and the residue crystallised from acetic acid. 2-Benzenesulphonamido-1 : 4-dichloronaphthalene was obtained.

Reactions of Compound B.—(i) With pyridine it gave a yellow solution decomposed by dilute hydrochloric acid to yield 2-benzenesulphonamido-1 : 4-dichloronaphthalene (above) and a solution from which only impure pyridinium compounds were obtained. (ii) Compound B reacted vigorously with aniline to give 3-*anilino*-2-*benzenesulphonamido*-1-*bromo*-4-*chloronaphthalene*, which, after repeated crystallisation from acetic acid to eliminate violet impurities, formed needles, m. p. 195—196° (Found: C, 55·2; H, 3·4; N, 5·9. $C_{22}H_{16}O_2N_2SClBr$ requires C, 54·2; H, 3·3; N, 5·8%), hydrolysed by solution in cold sulphuric acid to yield 3-anilino-1-bromo-4-chloro-2-naphthylamine (*J.*, 1953, 3039).

Chlorination of 1-*Bromo*-2-*naphthylamine.*—Dry hydrogen chloride was passed slowly into a solution of the base (5 g.) in dry benzene (45 c.c.) until precipitation ceased. Dry chlorine (4·5 mols.) was then introduced, and the resulting green solution filtered from any unchanged hydrochloride and evaporated. The residual brown oil was dissolved in chloroform and by

progressive addition of light petroleum three compounds were obtained. The first, which formed prisms, m. p. 268—272°, from chloroform was, owing to its small amount, not examined further. The second and third *substances* separated from benzene in prisms, m. p. 158—161° (Found: C, 20·9; H, 1·5%) and 102—104° [Found: C, 30·7; H, 1·7. Compound (VIII), $C_{10}H_6NBrCl_{10}$, requires C, 20·9; H, 1·05. $C_{10}H_5NBrCl_5$ requires C, 30·3; H, 1·3%].

Thermal Decomposition of 1-*Bromo*-1 : 3 : 4-*trichloro*-1 : 2 : 3 : 4-*tetrahydro*-2-*toluene*-p-*sulphonimidonaphthalene*.—The compound decomposed at its m. p. with evolution of bromine and hydrogen halide (loss in wt., 18·7, 14·7%) and left a dark viscous mass, which slowly yielded crystalline material on treatment with hot acetic acid. After five recrystallisations needles, m. p. 181—183°, were obtained (0·2 g. from 2 g.) (Found: C, 44·7; H, 2·5%). This *substance* corresponds essentially to loss of hydrogen chloride (V; X = $SO_2{\cdot}C_7H_7$) ($C_{17}H_{12}O_2NSCl_2Br$ requires C, 45·8; H, 2·7%), and this product on reduction with zinc dust in acetic acid gave slightly impure 1 : 4-dichloro-2-toluene-*p*-sulphonamidonaphthalene. The decomposition is, however, complicated since the major part of the product is non-crystalline.

Interaction of 1 : 1 : 2 : 3 : 4-*Pentachloro*-1 : 2 : 3 : 4-*tetrahydro*-2-*acetonaphthalide* (VI) *with Aniline*.—The compound was added slowly to well-cooled aniline, and the resultant dark pasty mass dissolved in water and decomposed with dilute hydrochloric acid. On crystallisation of the red plastic mass so produced from ethanol slightly pink needles, m. p. 132° (decomp.), were obtained (Found: C, 56·3; H, 3·8. $C_{18}H_{15}ON_2Cl_3$ requires C, 56·6; H, 3·4%). On heating above the m. p. this *compound* vigorously evolved hydrogen chloride but no crystalline material could be obtained from the black, sticky residue. This reaction suggests that the compound is 2-acetamido-3-anilino-1 : 1 : 4-trichloro-1 : 4-dihydronaphthalene (VII).

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