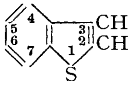
327. *Some Derivatives of Thionaphthen.*

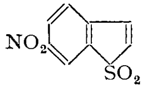
By FREDERICK CHALLENGER and PETER H. CLAPHAM.

Nitrothionaphthen sulphone is oxidised to 4-nitro-2-sulphobenzoic acid. The nitro-group is therefore in position (6). Mercuration of thionaphthen sulphone in methyl alcohol gives 2-acetoxymercuri-3-methoxy-2 : 3-dihydrothionaphthen sulphone. Methyl and ethyl alcohols in presence of the corresponding sodium alkoxides yield 3-alkoxy-2 : 3-dihydrothionaphthen sulphone, and hydriodic acid gives the corresponding iodo-compound. Dihydrothionaphthen sulphone is obtained by reduction of thionaphthen sulphone with zinc dust and sodium hydroxide.

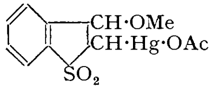
THE destruction of the aromatic system present in the thiophen ring of thionaphthen (I) would be expected to alter the position of substitution. Thionaphthen is nitrated in position 3, but we find that the nitrothionaphthen sulphone prepared by Lanfry (*Compt. rend.*, 1912, **154**, 519) is the 6-*nitro*-derivative (II), oxidation with potassium permanganate giving 4-nitro-2-sulphobenzoic acid which we find is also produced in small amount during the nitration. The acid, its *dimethyl* ester, and its cinchonine salt have been compared with authentic specimens obtained by oxidation of 4-nitrotoluene-2-sulphonic acid (Kastle, *Amer. Chem. J.*, 1889, **11**, 179; 1910, **44**, 485) during which process *p*-nitrobenzoic acid is also formed.



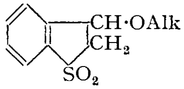
(I).



(II.)



(III.)



(IV.)

Thionaphthen is mercurated in the 3-position by mercuric acetate and methyl alcohol (Challenger and Miller, *J.*, 1939, **1005**) but we find that under comparable conditions the sulphone gives an addition product which is 2-*acetoxymercuri*-3-*methoxy*-2 : 3-*dihydrothionaphthen sulphone* (III), the $-CH{:}CH-SO_2-$ group exhibiting purely unsaturated properties. The position of the adducts is inferred from the established course of addition to unsaturated sulphones. The reaction is analogous to the well-known addition of mercury salts to ethylene and similar compounds. Where, as in 1 : 2-dihydronaphthalene and anethole the double bond is in the 1 : 2-position to the benzene nucleus, addition of mercuric acetate does not occur, but the compound is oxidised to a glycol (Straus and Lemmel, *Ber.*, 1921, **54**, 36). In the case of thionaphthen sulphone the 2 : 3-double bond is modified by the electrophilic properties of the $-SO_2-$ group. Like divinyl sulphone (Alexander and McCombie, *J.*, 1931, **1913**) and benzyl propenyl sulphone (Rothstein, *J.*, 1934, 684), thionaphthen sulphone forms addition *products* (IV) with alcohols in presence of sodium alkoxide and also with hydriodic acid. This was first observed in an attempt to reduce the sulphone with sodium and ethyl alcohol. Dihydrothionaphthen sulphone was, however, obtained by reduction with zinc dust and sodium hydroxide. Direct comparison with a specimen prepared from carefully purified dihydrothionaphthen (regenerated from its mercurichloride) by oxidation with potassium permanganate confirmed the m. p. 92° given by Fricke and Spilker (*Ber.*, 1925, **58**, 1594). It is difficult to explain the figure 98° given by von Braun, Bayer, and Kayser (*ibid.*, p. 2167). In the preparation of dihydrothionaphthen from nitrated phenylethyl chloride (see p. 1617) it is unnecessary to remove the whole of the *p*-compound before reduction and formation of the diazonium xanthate. This greatly simplifies the procedure.

Dihydrothionaphthen and its sulphone appear to give the same mononitro-derivative with nitric acid (*d* 1·5).

EXPERIMENTAL.

Nitration of Thionaphthen Sulphone.—The sulphone was prepared by Lanfry's method (*loc. cit.*; see also Weissgerber and Krüber, *Ber.*, 1920, **53**, 1554). The yield was 12 g. from 10 g. of thionaphthen and the diluted glacial acetic acid–hydrogen peroxide gave only a slight turbidity with barium chloride. The sulphone (10 g.) was gradually added to nitric acid (*d* 1·5; 30 c.c.) cooled by water, and left at room temperature for 3 hours. Pouring into water gave a pinkish-yellow solid (12·5 g., m. p. 184°). After three crystallisations from benzene the m. p. was 188°, unchanged on crystallisation from glacial acetic acid. If the temperature during nitration rose above about 15° only a red tar was obtained. The benzene mother-liquors yielded only the nitrosulphone and a small amount of brown resin (Found: C, 45·9; H, 2·6; N, 6·0. Calc. for $C_8H_5O_4NS$: C, 45·5; H, 2·4; N, 6·6%).

Nitrothionaphthen sulphone dibromide was prepared from its constituents in glacial acetic acid. After 18 hours, dilution with water gave a yellow solid, m. p. 145°, which was recrystallised (charcoal) from aqueous alcohol and from benzene–ligroin; m. p. 149—150° (Found: C, 26·1; H, 1·4; Br, 42·9, $C_8H_5O_4NBr_2S$ requires C, 25·9; H, 1·35; Br, 43·1%).

Oxidation of Nitrothionaphthen Sulphone. Orientation of the Nitro-group.—The nitro-sulphone (5 g.) was suspended in a solution of potassium hydroxide (4 g.) in water (500 c.c.), and solid potassium permanganate (12 g.) gradually added until slight excess was present. This was removed by hydrogen peroxide, and the filtered solution neutralised with dilute hydrochloric acid and concentrated till a neutral potassium salt separated on cooling. The solution was then strongly acidified, whereupon the acid potassium salt of 4-nitro-2-sulphobenzoic acid separated (5·5 g., 76%). This was recrystallised from water, air-dried, and titrated with standard alkali (phenolphthalein) (Found: *M*, 307, 308; loss at 150°, 6·1. Calc. for $C_7H_4O_7NSK,H_2O$: *M*, 303; H_2O, 5·95%).

The neutral potassium salt gave a cinchonine salt (not analysed) which on crystallisation from water had the unsharp but constant m. p. of 165—170° alone and in admixture with a sample of identical m. p. prepared from authentic dipotassium 4-nitro-2-sulphobenzoate.

The acid potassium salt in hot water was treated with barium chloride solution, and neutralised by barium carbonate paste. The salt which separated was suspended in hot water, dissolved by addition of dilute hydrochloric acid, barium removed by sulphuric acid, and the filtrate concentrated till the acid crystallised on cooling. Dried on tile, this had m. p. 70°, and after heating at 80° for several hours, 144°. A few minutes' exposure to air lowered the m. p. by several degrees. A sample of m. p. 142° had mixed m. p. 144° with authentic 4-nitro-2-sulphobenzoic acid, m. p. 145°. A second oxidation of the nitrated sulphone gave a specimen of this acid which had m. p. and mixed m. p. 140—142°, with a known sample of the same m. p. The *dimethyl* ester was prepared by means of diazomethane, and, crystallised from benzene–light petroleum, had m. p. 114—115° alone and when mixed with an authentic sample of the same m. p. (Found: C, 39·4; H, 3·3; S, 11·8. $C_9H_9O_7NS$ requires C, 39·3; H, 3·3; S, 11·6%).

Oxidation during Nitration of Thionaphthen Sulphone.—The spent acid was concentrated, and traces of white solid removed, m. p. 206°. This was insufficient for crystallisation but probably consisted of impure *p*-nitrobenzoic acid resulting from elimination of the sulpho-group from 4-nitro-2-sulphobenzoic acid. On evaporation to a syrup, this sulphonic acid crystallised on cooling. When dried as before it melted at 140° and gave a dimethyl ester, m. p. 114—115°.

Preparation of Authentic 4-*Nitro*-2-*sulphobenzoic Acid and its Dimethyl Ester. Hydrolysis of the Sulpho-group.*—The potassium salt of 4-nitrotoluene-2-sulphonic acid was prepared by Kastle's method (*loc. cit.*, 1910) from *p*-nitrotoluene, and this (10 g.) was oxidised by warming with alkaline permanganate. The 4-nitro-2-sulphobenzoic acid was isolated as the acid potassium salt (9·5 g.), which was converted into the free acid by the method already described. This had m. p. about 70° when dried on tile (71·2°; Hausser, *Bull. Soc. chim.*, 1891, **6**, 391), and after several hours' heating at 80° the m. p. was 144° (146°; Hausser, *loc. cit.*). The dimethyl ester, prepared by the action of ethereal diazomethane on the anhydrous acid, had m. p. 114—115° (Found : C, 39·8; H, 3·3; S, 11·8%).

During the concentration of the aqueous solution of the sulphonic acid a small amount of white solid was deposited, m. p. 238°. This was obtained in larger quantity (0·25 g.) when the *alkaline* solution of the acid was concentrated before the isolation of the acid potassium salt. Recrystallised from benzene, it had m. p. 238—239° and mixed m. p. 238—239° with a known specimen of *p*-nitrobenzoic acid of the same m. p. The *p*-nitrobenzyl ester had m. p. 168° and mixed m. p. 168° with an authentic specimen of the same m. p.

Reduction of Thionaphthen Sulphone.—After treatment of the sulphone with zinc dust and acetic acid and with sodium amalgam and water it was recovered unchanged. When finely ground and heated at 100° with excess of zinc dust and aqueous sodium hydroxide, the solid gradually melted to a colourless oil. After 2 hours, water was added and the mixture boiled till the oil dissolved. On filtration and concentration, crystals separated, m. p. 90—91° and 92° on crystallisation from water, unchanged on further crystallisation from water or ligroin (A). The mixed m. p. with authentic dihydrothionaphthen sulphone (B) was 92° (see below) (Found : C, 57·0; H, 4·9; S, 19·0. Calc. for $C_8H_8O_2S$: C, 57·1; H, 4·8; S, 19·0%).

Reactivity of the Double Bond in Thionaphthen Sulphone. Ethoxydihydrothionaphthen Sulphone.—In an earlier attempt to reduce the sulphone, 2·5 g. in ethyl alcohol (50 c.c.) were gradually treated with sodium (1 g.) in thin slices. The orange solution on dilution with water gave 1·8 g. of a white solid, m. p. 106° and 107—108° after crystallisation from water, alcohol, or benzene–petrol. Repeated operations failed to alter the m. p. of the *product* (Found : C, 56·7; H, 5·8; S, 15·5; OEt, by Zeisel, 21·9. $C_{10}H_{12}O_3S$ requires C, 56·6; H, 5·7; S, 15·1; OEt, 21·2%). The slightly high value for ethoxyl is due to the formation of traces of silver sulphide.

Methoxydihydrothionaphthen Sulphone.—When the experiment was repeated but with methyl alcohol as solvent, the *product* melted at 77—78° after crystallisation from water (Found : OMe, 16·4. $C_9H_{10}O_3S$ requires OMe, 15·7%).

Addition of Hydrogen Iodide at the Double Linkage. Iododihydrothionaphthen Sulphone.—The sulphone was warmed with excess of hydriodic acid (*d* 1·9) for 3 hours. Dilution with water gave a dark oil which was well washed with water and solidified on rubbing with alcohol. The *iodo*-compound crystallised from alcohol in colourless needles, m. p. 104—105° (Found : I, 43·3. $C_8H_7O_2IS$ requires I, 43·5%).

Reduction with sodium amalgam and water in the cold gave thionaphthen sulphone, m. p. 142°, and not its dihydro-derivative.

Mercuration of Thionaphthen Sulphone.—The sulphone (2 g.) in methyl alcohol (80 c.c.) was heated for 5 days with a solution of yellow mercuric oxide (8 g.) in glacial acetic acid (10 c.c.) and water (60 c.c.). Some mercurous acetate separated. On filtration, removal of methyl alcohol, and dilution with water, a solid slowly separated, m. p. 144°. On recrystallisation from aqueous alcohol, this *acetoxymercuri*-compound formed shining needles, m. p. 151—153° (Found : Hg, 44·0, 44·0; OMe, 6·7. $C_{11}H_{12}O_5SHg$ requires Hg, 44·1; OMe, 6·8%. The hydroxy-addition product $C_{10}H_{10}O_5SHg$ requires Hg, 45·3%). Hydrogen sulphide in aqueous solution gives mercuric sulphide; hydrochloric acid regenerates the sulphone; bromine and hydrogen bromide in cold glacial acetic quickly give thionaphthen sulphone dibromide, m. p. and mixed m. p. 164—165° (Lanfry, *loc. cit.*).

Alternative Preparations of Dihydrothionaphthen Sulphone.—Dihydrothionaphthen was prepared by the method of von Braun, Bayer, and Kayser (*loc. cit.*; see also Ferber, *ibid.*, 1929, **62**, 183; Bennett and Hafez, *J.*, 1941, 287). Phenylethyl chloride was nitrated (Barger, *J.*, 1909, **95**, 2194) and as much as possible of the solid *p*-nitro-compound removed. The liquid portion, containing also the *o*-derivative and traces of the *m*-compound (Holleman and Hoeflake, *Rec. Trav. chim.*, 1915, **34**, 261), was reduced (Ferber, *loc. cit.*), diazotised, and converted by the xanthate method and ring-closure into dihydrothionaphthen (the isomeric amines did not interfere). The crude product (C), b. p. 110—111°/18 mm. (v. Braun *et al.* give 104°/13 mm.), was twice fractionated giving (D) of b. p. 110—111°/18 mm. (Found : C, 71·3; H, 6·3; Calc. for C_8H_8S : C, 70·6; H, 5·9%). This with potassium permanganate gave a sulphone (B) of m. p. 92° (Found : C, 56·8; H, 4·9; S, 19·4. Calc. for $C_8H_8O_2S$: C, 57·1; H, 4·8; S, 19·0%). (D) was converted into the mercurichloride, m. p. 128° (Fricke and Spilker, *loc. cit.*), from which the dihydrothionaphthen was regenerated by dilute hydrochloric acid and converted into sulphone (E) as before, m. p. 92°. Fricke and Spilker (*loc. cit.*) give m. p. 91·5—92° (uncorr.); v. Braun *et al.*, and Bennett and Hafez found m. p. 98°. Preparations (A) (see above) and (B) were of entirely different origin, and (E) was obtained by a rigorous purification of (D). They all melted constantly at 92°.

Nitration of Dihydrothionaphthen and of its Sulphone.—Dihydrothionaphthen (0·5 g.) was added dropwise to cooled nitric acid (*d* 1·5), and the solution poured on ice. No solid separated, and the mixture was evaporated to a syrup. This partially solidified on being washed with sodium carbonate. When washed with methyl alcohol and recrystallised from aqueous alcohol, it melted at 142°. In admixture with thionaphthen sulphone (m. p. 142°) the m. p. was depressed. The quantity was too small for analysis but the compound probably consisted of mononitrodihydrothionaphthen sulphone. Dihydrothionaphthen sulphone (specimen B) was dissolved in nitric acid (*d* 1·5) and left for a short time at room temperature. Dilution with water gave colourless plates, m. p. 143°, on recrystallisation from alcohol (Found: C, 44·9; H, 3·2; N, 6·7. $C_8H_7O_4NS$ requires C, 45·3; H, 3·3; N, 6·6%). The same *compound*, m. p. and mixed m. p. 143°, was obtained on nitration of specimen (A).

The authors thank Imperial Chemical Industries Ltd. for a grant and the Trustees of the Brotherton Scholarship for an award to P. H. C.

THE UNIVERSITY, LEEDS.

[*Received, October* 22*nd*, 1947.]