857. *Some Reactions of Naphtho*[2,3-b]*thiophen.*

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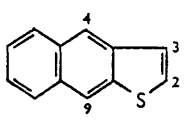
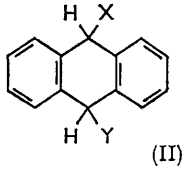
Naphtho[2,3-*b*]thiophen (I) forms *meso*-addition compounds much less readily than anthracene does, but a maleic anhydride adduct can be made under forcing conditions. Reduction with sodium and pentyl alcohol gives the 4,9- and the 2,3-dihydro-compound. Friedel–Crafts acetylation in nitrobenzene leads to the 3-acetyl compound; in methylene chloride a mixture containing the 3- and the 4-acetyl derivative is obtained.

The ultraviolet absorption spectrum of naphtho[2,3-*b*]thiophen [1] (I) is similar to that of anthracene, but is shifted to shorter wavelengths. It seemed of interest to determine if there were any similarities in the chemistry of the two compounds.

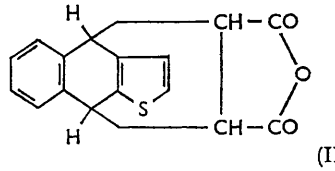
Anthracene and the higher acenes readily form addition compounds of type (II) with a variety of agents; [2] with oxygen in presence of light they give photo-oxides and they react rapidly with dienophiles. Anthracene also readily forms a photo-dimer. In contrast, naphtho[2,3-*b*]thiophen (I) shows very little tendency to form stable addition products.



(I)



(II)



(III)

No photo-dimer was produced when a benzene solution of the naphthothiophen was irradiated with light from a tungsten filament or with summer sunshine. The compound was recovered after prolonged irradiation of a solution in carbon disulphide in presence of oxygen, and exposure of an ethanolic solution to sunlight and air [3] gave the quinone but no oxide. The naphthothiophen also failed to react with dehydrobenzene, which it was hoped, by analogy with the reaction of anthracene,[4] would lead to a thiophen analogue of triptycene. An attempted Diels–Alder reaction with tetracyanoethylene, which proceeds very rapidly with anthracene,[5] was also unsuccessful; a coloured intermediate was formed in solution, but no adduct could be isolated. With an equimolecular amount

[1] Carruthers and Crowder, *J.*, 1957, 1932.
[2] For a summary of these reactions see Badger, " The Structures and Reactions of Aromatic Compounds," Cambridge University Press, 1954, Chapters 4, 8, and 9.
[3] Cf. Southern and Waters, *J.*, 1960, 4340.
[4] Wittig and Benz, *Chem. Ber.*, 1958, **91**, 882; Wittig, Knauss, and Neithammer, *Annalen*, 1960, **630**, 10.
[5] Middleton, Heckert, Little, and Krespan, *J. Amer. Chem. Soc.*, 1958, **80**, 2783.

of maleic anhydride in boiling xylene the adduct (III) was obtained in less than 10% yield; anthracene, under the same conditions, reacts almost quantitatively.[6] The adduct (III) was produced in high yield, with a large excess of maleic anhydride in benzene. Its ultraviolet spectrum showed no absorption above 280 mμ, and in agreement with its structure, is essentially a summation of the spectra of tetralin and thiophen. Reduction of the naphthothiophen with sodium and pentyl alcohol afforded the 4,9-dihydro-compound and, in smaller amount, the known [7] 2,3-dihydro-compound, in addition to some unidentified minor products. The structure of the 4,9-dihydro-isomer is based on its ultraviolet absorption spectrum, which is similar to that of the maleic anhydride adduct (III). Both compounds show four strong bands in the aromatic C–H out-of-plane deformation region of the infrared spectrum. In this reaction the naphthothiophen resembles both anthracene [8] and benzo[*b*]thiophen [9] which are converted into the 9,10- and the 2,3-dihydro-compound, respectively, with sodium and alcohol. Reduction of naphthothiophen with di-imide [10] also afforded a small yield (8—10%) of a substance which appears to be the 2,3-dihydro-compound (by vapour-phase chromatography), but it was not obtained completely free from starting material and its identification is uncertain.

Bromination of the naphthothiophen afforded only substitution products, and no addition compound corresponding to the dibromodihydroanthracene (II; X = Y = Br).[11] With one mol. of bromine a single monobromo-derivative was obtained which must be either the 4- or the 9-isomer for it was converted into the bromine-free 4,9-quinone on oxidation with chromium trioxide. With two mol. of bromine 4,9-dibromonaphtho-[2,3-*b*]thiophen was produced; this likewise gave the 4,9-quinone on oxidation. Bromination of anthracene in presence of pyridine leads to the 9,10-dihydro-9,10-dipyridino-derivative dibromide; [12] with naphthothiophen no pure product was obtained, but the crude material showed typical naphthothiophen-type ultraviolet absorption and is evidently not an addition product.

Friedel–Crafts acetylation of naphthothiophen was strongly influenced by the solvent. In nitrobenzene a single crystalline ketone was obtained in high yield. This was converted by Clemmenson reduction into the ethyl derivative, whence desulphurisation with Raney nickel to 2-s-butylnaphthalene identified the ketone as 3-acetylnaphthothiophen. In methylene chloride the 3-acetyl derivative was again produced, but the main product was an oil which consisted largely of 4-acetylnaphthothiophen with a small amount of a third product detected by vapour-phase chromatography but not isolated. Oxidation of the pure 4-acetyl derivative afforded naphthothiophen-4,9-quinone and by Clemmensen reduction and desulphurisation with Raney nickel it was converted into 1,2-diethyl-naphthalene. Curiously, Clemmensen reduction of the 4-acetyl compound gave a considerable amount of 4-ethyl-2,3-dihydronaphthothiophen, identified by its ultraviolet spectrum, as well as the expected 4-ethyl derivative. No comparable product was detected in the Clemmensen reduction of the 3-acetyl compound, where it was perhaps more to be expected, and naphthothiophen itself was unaffected by the same conditions. A small amount of naphthothiophen was also isolated from the Clemmensen reaction, evidently produced by deacylation, for the ketone used was shown by vapour-phase chromatography to be completely free from the parent compound. Deacylation of 9-acylanthracenes with acid has been reported.[13] The almost exclusive formation of the 3-acetyl compound by Friedel–Crafts acetylation of naphthothiophen in nitrobenzene, in contrast to the *meso*-compounds produced by bromination, is presumably due to steric hindrance to attack

[6] Bachmann and Kloetzel, *J. Amer. Chem. Soc.*, 1938, **60**, 481.
[7] Carruthers, Douglas, and Hill, *J.*, 1962, 704.
[8] Bamberger and Lodter, *Ber.*, 1887, **20**, 3073.
[9] Fricke and Spilker, *Ber.*, 1925, **58**, 1589.
[10] Corey, Mock, and Pasto, *Tetrahedron Letters*, 1961, 347; Van Tamelen, Dewey, Lease, and Pirkle, *J. Amer. Chem. Soc.*, 1961, **83**, 4302.
[11] Barnett and Cook, *J.*, 1924, **125**, 1084.
[12] Barnett and Cook, *J.*, 1921, **119**, 901.
[13] Cook, *J.*, 1926, 1282; Krollpfeiffer, *Ber.*, 1923, **56**, 2360.

at the *meso*-positions by the bulky solvated aluminium chloride complex present in nitrobenzene solution.[14] In methylene chloride the smaller size of the complex allows predominant attack at the more reactive 4-position. A similar effect of the solvent has been noted in Friedel–Crafts acetylation of naphthalene,[14] chrysene,[15] and anthracene.[16] It was conceivable that in both solvents some of the 3-acetyl compound was produced by isomerisation of the initially formed 4-isomer. Isomerisation of 9-acetylanthracene to the 1- and the 2-isomer is brought about readily by aluminium chloride,[16] and the deacetylation of 4-acetylnaphtho[2,3-*b*]thiophen during Clemmensen reduction shows that the acetyl group is mobile under acid conditions. But 4-acetylnaphtho[2,3-*b*]thiophen was practically unaffected by treatment with aluminium chloride in nitrobenzene solution for eighteen hours, and there was no significant difference in the proportion of the two isomers formed by acetylation in methylene chloride for 1 hour and for 24 hours. Direct attack at position 3 rather than migration thus seems more likely.

The greater difficulty in preparing *meso*-addition compounds of naphthothiophen than of anthracene is in line with the hypsochromic shift in the ultraviolet spectrum of the sulphur compound, and with the higher oxidation–reduction potential of the quinone [17] than of anthraquinone (ref. 2, pp. 87 *et seq.*). Naphtho[2,3-*b*]thiophen may be considered as a lower member of the series formed by anthracene and the higher acenes, which show a shift of the ultraviolet absorption to longer wavelengths and increased reactivity with increase in the number of fused rings. The " order number " of naphthothiophen, calculated from the frequency of the longest-wavelength absorption band according to Clar,[18] is 7·76, intermediate between those of naphthalene and anthracene, in line with the chemical behaviour of the compound. The calculated (ref. 18, p. 43) oxidation–reduction potential of the quinone (0·254 v) is in good agreement with the experimental value (0·250 v).[17] The close correspondence in the melting points of the naphthothiophen derivatives and the anthracene isosteres is also noteworthy.

Experimental

M. p.s were determined on a Kofler block, and vapour-phase chromatography experiments were done at 175° with Apiezon L grease (0·1% on glass beads) as stationary phase, unless otherwise stated. Ultraviolet absorption spectra refer to solutions in 95% ethanol. Light petroleum refers to the fraction of b. p. 60—80°.

Maleic Anhydride Adduct of Naphtho[2,3-b]*thiophen.*—A solution of freshly distilled maleic anhydride (3·1 g.) and naphtho[2,3-*b*]thiophen (0·2 g.) in dry benzene (4 ml.) was boiled for 48 hr. Benzene and some of the excess of maleic anhydride were removed on the water-bath under reduced pressure, and the solid was ground and extracted with warm water. The residue was heated on the water-bath for 2 hr. with 5% aqueous potassium hydroxide (10 ml.), and the cooled alkaline solution was extracted with ether to remove naphtho[2,3-*b*]thiophen (22 mg.). Acidification gave the *adduct* (III) (190 mg.) which crystallised from ethyl acetate containing a few drops of acetic anhydride as prisms. The m. p. depended on the rate of heating; when heated slowly from room temperature the adduct melted at 193—195° (Found: C, 67·8; H, 3·65. $C_{16}H_{16}O_3S$ requires C, 68·1; H, 3·6%); $\lambda_{max.}$ were at 235—240 (shoulder) and (270) * mμ [log ε 3·68 (2·92)], $\nu_{max.}$ (KBr disc) at 1780 and 1860 (anhydride), 840, 760 (1,2-disubstituted benzene ring), 725, 675 cm.$^{-1}$.

When a solution of the naphthothiophen (100 mg.) and maleic anhydride (48 mg., 1 mol.) in xylene (2 ml.) was boiled for 6 hr. (cf. Bachmann and Kloetzel [6]) 89 mg. of naphthothiophen

* Parentheses denote inflexions.

[14] Baddeley, *J.*, 1949, S.1, 99.
[15] Carruthers, *J.*, 1953, 3486.
[16] Gore, *J. Org. Chem.*, 1957, **22**, 135; Hawkins, *J.*, 1957, 3858; Bassilios, Shawky, and Salem, *Rec. Trav. chim.*, 1962, **81**, 679.
[17] Fieser and Ames, *J. Amer. Chem. Soc.*, 1927, **49**, 2604.
[18] Clar, " Aromatische Kohlenwasserstoffe," Springer-Verlag, Berlin, 1941, pp. 20 *et seq.*

were recovered; the recovered acidic material (12 mg.), crystallised from ethyl acetate–acetic anhydride, gave the adduct (III) (2 mg.), m. p. and mixed m. p. 190—192°. Catalysis with aluminium chloride [19] gave coloured material which appeared to contain adduct (infrared spectrum), but no pure product could be isolated.

Bromination of Naphtho[2,3-b]*thiophen.*—(*a*) Bromine (98 mg.) in carbon tetrachloride (1 ml.) was added to a suspension of naphtho[2,3-*b*]thiophen (108 mg.) in carbon tetrachloride (3 ml.) at −10°. Hydrogen bromide was evolved and after 45 min. the colour of the bromine was discharged and the suspension had dissolved. The solvent was removed under a vacuum at room temperature and the residue, which had ultraviolet absorption identical with that of the pure product in position and intensity, was chromatographed on alumina. Elution with light petroleum gave 4(or 9)-*bromonaphtho*[2,3-b]*thiophen* as silky needles, m. p. 96—98° (from cyclohexane) (Found: C, 54·3; H, 3·0. $C_{12}H_7BrS$ requires C, 54·75; H, 2·7%), $\lambda_{max.}$ 253, 261, (322), 345, (358), 362 mμ [log ε 4·79, 4·83, (3·62), 3·89, (3·85), 4·03]. Vapour-phase chromatography at 210° on 5% of Dow 11 silicone gum supported on firebrick showed only one peak. Oxidation of this product (40 mg.) with chromium trioxide (100 mg.) in acetic acid (4 ml.) afforded naphtho[2,3-*b*]thiophen-4,9-quinone (27 mg.), m. p. and mixed m. p. 230—232°.

Later eluates of the chromatogram gave small amounts of the dibromo-compound described below.

(*b*) A solution of naphtho[2,3-*b*]thiophen (150 mg.) in carbon disulphide (5 ml.) was treated at 0° with a solution of bromine (260 mg., 2 mol.) in carbon disulphide (5 ml.). Hydrogen bromide was evolved. After 2 hr. solvent and the excess of bromine were removed under a vacuum, and the residue was crystallised from methanol–benzene. 4,9-*Dibromonaphtho*-[2,3-b]*thiophen* (40 mg.) was obtained as silky needles, m. p. 193—195° (Found: C, 42·1; H, 2·0. $C_{12}H_6Br_2S$ requires C, 42·1; H, 1·8%), $\lambda_{max.}$ 254, 261, (325), (335), 350, (365), 368 mμ [log ε 4·82, 4·86, (3·63), (3·79), 3·93, (3·95), 4·09]. Material from the mother-liquors gave two peaks on vapour-phase chromatography, corresponding to the 4,9-dibromo-compound and the mono-bromo-compound described above.

Oxidation of the dibromo-compound (30 mg.) with chromium trioxide (100 mg.) in acetic acid (4 ml.) gave naphtho[2,3-*b*]thiophen-4,9-quinone, m. p. and mixed m. p. 227—229°.

Attempted Photodimerisation and Photo-oxidation of Naphtho[2,3-b]*thiophen.*—(*a*) A solution of naphtho[2,3-*b*]thiophen (100 mg.) in benzene (5 ml.) was irradiated under nitrogen in a Pyrex glass vessel with light from an 80-w electric light bulb from which the glass envelope had been removed. Under these conditions anthracene photo-dimer (52 mg.) was produced from anthracene (100 mg.) within 1 hr. After 120 hr. the green solution was filtered from a small amount of black solid and evaporated. Crystallisation from ethanol gave naphtho[2,3-*b*]-thiophen (70 mg.), m. p. and mixed m. p. 196—198°. Less pure material, m. p. 189—196°, was obtained from the mother-liquors.

(*b*) A solution of naphtho[2,3-*b*]thiophen (30 mg.) in benzene (1·5 ml.) in a sealed tube under nitrogen was illuminated by summer sunshine during 28 days. Evaporation and crystallisation gave crystals, m. p. 197—199° alone or mixed with naphtho[2,3-*b*]thiophen. The infrared and ultraviolet spectra were identical with those of naphthothiophen. In one experiment a minute amount of a crystalline substance insoluble in hot benzene was obtained, having m. p. 196—199°, $\lambda_{max.}$ 246 mμ (log ε 3·79). This may have been a dimer but attempts to prepare larger amounts were fruitless.

(*c*) A solution of naphtho[2,3-*b*]thiophen (30 mg.) in carbon disulphide (5 ml.) was irradiated with artificial light, as above, in an atmosphere of oxygen for 120 hr. The crude product had an infrared spectrum identical with that of starting material and by chromatography on alumina [3] yielded only naphtho[2,3-*b*]thiophen (27 mg.), m. p. and mixed m. p. 196—198°.

In another experiment a solution of naphtho[2,3-*b*]thiophen (50 mg.) in ethanol was exposed to air and sunlight for 3 weeks in a vessel protected from rain (cf. Southern and Waters [3]). Ethanol was added from time to time to keep the material in solution. The recovered brown gum was chromatographed on alumina; elution with light petroleum–benzene (1 : 1) afforded naphtho[2,3-*b*]thiophen, m. p. and mixed m. p. 196—198°, and then the 4,9-quinone, m. p. 225° alone or mixed with authentic material.

Attempted Reaction of Naphtho[2,3-b]*thiophen with Dehydrobenzene.*—A solution of *o*-fluoro-bromobenzene (260 mg.) in tetrahydrofuran (3 ml.) was added to magnesium (54 mg.) in a

[19] Yates and Eaton, *J. Amer. Chem. Soc.*, 1960, **82**, 4436; Fray and Robinson, *ibid.*, 1961, **83**, 249.

solution of naphthothiophen (500 mg.) in tetrahydrofuran (6 ml.) under nitrogen. The mixture was boiled for 48 hr. and poured into methanol. The precipitate was collected and dissolved in benzene, the washed solution (dilute sulphuric acid and water) dried and evaporated, and the product chromatographed on alumina. Elution with light petroleum–benzene (1 : 1) gave naphthothiophen (370 mg.), identified by mixed m. p. Later fractions afforded gum which was rechromatographed. Ultraviolet absorption measurements of the eluates showed the presence of naphthothiophen and of triphenylene, but none of the fractions examined gave evidence of an addition product.

Reduction with Sodium and Pentyl Alcohol.—Sodium (160 mg.) was added to a hot solution of naphtho[2,3-*b*]thiophen (300 mg.) in pentyl alcohol (4 ml.). After 30 min. the alcohol was removed under a vacuum, the residue was dissolved in benzene–water, and the layers were separated. Acidification of the alkaline solution gave a brown gum (50 mg.) which was not further examined. Evaporation of the washed (water) and dried benzene layer afforded a solid product (240 mg.) shown by vapour-phase chromatography to contain three main components and small amounts of at least three others, one of which was probably starting material; the exact composition differed in different experiments. By chromatography on alumina and elution with light petroleum the main component, 4.9-*dihydronaphtho*[2,3-b]*thiophen* (56 mg.) was obtained as blades, m. p. 104—105° (from light petroleum, b. p. 40—60°) (Found: C, 76·9; H, 5·9. $C_{12}H_{10}S$ requires C, 77·4; H, 5·4%), $\lambda_{max.}$ 230 (sh), 246 (sh) mμ (log ε 3·90, 3·74). The infrared spectrum had four strong maxima in the 650—900 $cm.^{-1}$ region similar to those in the spectrum of the maleic anhydride adduct. Further elution with light petroleum containing increasing amounts of benzene gave mixtures and then 2,3-dihydronaphtho[2,3-*b*]thiophen (40 mg.), m. p. and mixed m. p. 138—140° (the m. p. of the 2,3-dihydro-compound is 139—141°, not 149—151° as reported [7]), $\lambda_{max.}$ 249, 255, 274, 284, 294, 326, 328 mμ (log ε 4·58, 4·58, 3·92, 3·98, 3·84, 3·47, 3·52). The infrared spectrum (KBr disc) was identical with that of authentic material, and showed two strong maxima at 871 and 747 $cm.^{-1}$ as expected for a 2,3-disubstituted naphthalene derivative.[20]

Friedel–Crafts Acetylation.—(*a*) *In nitrobenzene solution.* A suspension of naphtho[2,3-*b*]-thiophen (360 mg.) in nitrobenzene (5 ml.) was added to a solution of aluminium chloride (320 mg.) and acetyl chloride (0·2 ml.) in nitrobenzene (5 ml.). The dark red mixture was stirred for 20 hr. and then ice was added and nitrobenzene removed with steam. The residue was extracted with benzene and afforded 368 mg. of dark gum. Vapour-phase chromatography of this gave only one major and two very minor (about 2%) peaks, one of which had retention time similar to that of 4-acetylnaphtho[2,3-*b*]thiophen (below). By chromatography on alumina and elution with light petroleum–benzene (1 : 1) 3-*acetylnaphtho*[2,3-b]*thiophen* (250 mg.) was obtained as needles, m. p. 126—127° (from ethanol–benzene) (Found: C, 74·4; H, 4·6. $C_{14}H_{10}OS$ requires C, 74·3; H, 4·5%), $\lambda_{max.}$ 244, (266), (304), 318, 332, 356—360 mμ [log ε 4·92, (4·18), (3·35), 3·51, 3·70, 3·82], $\nu_{max.}$ (in Nujol) 1660 $cm.^{-1}$. Oxidation of this compound with sodium hypoiodite [21] gave the 3-*carboxylic acid*, needles, m. p. 268—270° (from ethanol–benzene) (Found: C, 68·1; H, 3·6. $C_{13}H_8O_2S$ requires C, 68·4; H, 3·5%), $\lambda_{max.}$ 238, (244), 311, 324, 342, 353 mμ [log ε 4·80, (4·75), 3·57, 3·75, 3·75, 3·76].

The ketone (200 mg.), amalgamated zinc (1 g.), hydrochloric acid (5 ml.), water (1 ml.), acetic acid (3 ml.), and toluene (2 ml.) were boiled for 48 hr. The cooled mixture was extracted with benzene, and the crude product was chromatographed on alumina. 3-*Ethylnaphtho*-[2,3-b]*thiophen* was eluted with light petroleum and had b. p. 205—210°/1 mm. (air-bath temp.) (Found: C, 79·5; H, 5·7. $C_{14}H_{14}S$ requires C, 79·2; H, 5·7%), $\lambda_{max.}$ (253), 257, 337, 353 mμ [log ε (4·92), 4·96, 3·78, 3·88]. It gave only one peak on vapour-phase chromatography. The *picrate* formed deep red needles, m. p. 118° (from ethanol) (Found: C, 54·4; H, 3·5. $C_{14}H_{14}S,C_6H_3N_3O_7$ requires C, 54·4; H, 3·4%).

The compound (290 mg.) was desulphurised with Raney nickel (1 g.) in boiling ethanol for 2 hr. The crude product was chromatographed on alumina, and gave 2-s-butylnaphthalene (80 mg.) as an oil with infrared and ultraviolet spectra identical with those of authentic material. {$\lambda_{max.}$ 225, (260), 266, 270, 276, (286), 306, 313, 321 mμ [log ε 5·03, (3·60), 3·67, 3·71, (3·55), 2·82, 2·70, 2·86]}. Vapour-phase chromatography at 125° showed the presence of about 7% of impurity. The picrate formed orange-yellow needles, m. p. 70—73° not depressed when

[20] Werner, Kennard, and Rayson, *Austral. J. Chem.*, 1958, **8**, 346.
[21] Fuson and Tulloch, *J. Amer. Chem. Soc.*, 1934, **56**, 1638.

mixed with an authentic specimen (m. p. 67—71°; lit., 60—64°, 64—68°), and the *s*-trinitrobenzene complex gave yellow needles, m. p. and mixed m. p. 81—84°. Contrary to a report [22] the trinitrobenzene complex crystallises from ethanol.

(*b*) *In methylene chloride solution.* A solution of naphtho[2,3-*b*]thiophen (3 g.) in methylene chloride (80 ml.) was added to a solution of aluminium chloride (2·6 g.) and acetyl chloride (1·6 ml.) in methylene chloride (100 ml.) cooled in ice. The dark red solution was kept at room temperature for 18 hr. with stirring, and then ice and hydrochloric acid were added. The recovered neutral oil (3·8 g.) gave two main peaks on vapour-phase chromatography in the approximate ratio of 2 : 5; the lesser had retention time corresponding to the 3-acetyl compound. There were also two minor peaks, one of which was probably due to naphthothiophen. Chromatography on alumina and elution with light petroleum containing increasing proportions of benzene afforded an oil (900 mg.) and then 3-acetylnaphtho[2,3-*b*]thiophen (790 mg.), m. p. and mixed m. p. 121—123°. The oil was rechromatographed and gave 4-*acetylnaphtho*[2,3-b]-*thiophen*, b. p. 160—165°/0·8 mm. (air-bath temp.) (Found: C, 74·7; H, 4·4. $C_{14}H_{10}OS$ requires C, 74·3; H, 4·45%), $\lambda_{max.}$ 236, 260, 344, 359 mμ (log ε 4·12, 4·66, 3·70, 3·79), $\nu_{max.}$ 1660 cm.$^{-1}$. Vapour-phase chromatography of this material gave only one peak with the same retention time as the major peak from the crude product. The 2,4-dinitrophenylhydrazone formed orange-red prisms, m. p. 250—256° (in benzene). Oxidation of the ketone (50 mg.) with chromium trioxide (50 mg.) in acetic acid (2 ml.) gave naphthothiophen-4,9-quinone, m. p. and mixed m. p. 228—230°.

The ketone (700 mg.), amalgamated zinc (5 g.), concentrated hydrochloric acid (25 ml.), water (5 ml.), acetic acid (15 ml.), and toluene (10 ml.) were boiled for 72 hr. Vapour-phase chromatography of the recovered neutral gum (660 mg.) showed that it contained three major components which were partially separated by chromatography on alumina. Elution with light petroleum–benzene (10 : 1) afforded two liquid fractions; further elution with light petroleum–benzene (3 : 2) gave naphtho[2,3-*b*]thiophen (25 mg.), m. p. and mixed m. p. 193—195°. The first liquid fraction was purified by rechromatography on alumina and by crystallisation of the picrate. 4-*Ethylnaphtho*[2,3-b]*thiophen* (47 mg.) was then obtained as an oil, b. p. 165—170°/0·5 mm. (air-bath temp.) (Found: C, 79·1; H, 5·65. $C_{14}H_{12}S$ requires C, 79·2; H, 5·7%), $\lambda_{max.}$ (237), 252, 259, (318), (333), 341, 357 mμ [log ε (4·10), 4·77, 4·78, (3·37), (3·77), 3·79, 3·81]. Vapour-phase chromatography showed one main component with about 5% of impurity. The *picrate* formed red needles (from ethanol), m. p. 99—101° (Found: C, 54·4; H, 3·7. $C_{14}H_{12}S,C_6H_3N_3O_7$ requires C, 54·3; H, 3·4%). The same procedure, applied to the second liquid fraction, gave 4-*ethyl*-2,3-*dihydronaphtho*[2,3-b]*thiophen* (40 mg.), b. p. 170°/0·5 mm. (air-bath temp.) (Found: C, 78·7; H, 6·6. $C_{14}H_{14}S$ requires C, 78·5; H, 6·6%), $\lambda_{max.}$ 253, 258, 279, 290, 302, 333, 345 mμ (log ε 4·54, 4·57, 3·80, 3·91, 3·81, 3·33, 3·39). It gave only one peak on vapour-phase chromatography. The *picrate* formed red needles (in ethanol), m. p. 100—101° (Found: C, 54·2; H, 3·9. $C_{14}H_{14}S,C_6H_3N_3O_7$ requires C, 54·3; H, 3·9%), only slightly depressed to 95—98° when mixed with the picrate of 4-ethylnaphthothiophen.

Desulphurisation of the 4-ethyl compound (50 mg.) with Raney nickel in boiling ethanol for 1 hr. and chromatography of the product on alumina afforded 1,2-diethylnaphthalene (18 mg.), identified by its infrared spectrum and by its picrate, m. p. and mixed m. p. 104—106°. Vapour-phase chromatography at 125° gave one main peak with retention time of 1,2-diethylnaphthalene, and a minor peak corresponding to 2-s-butylnaphthalene, derived from 3-acetylnaphthothiophen.

Similarly the 4-ethyl-2,3-dihydro-compound (100 mg.) with Raney nickel in boiling ethanol for 3 hr. gave 1,2-diethylnaphthalene (40 mg.), $\lambda_{max.}$ (225), 229, (266), 276, 285, (292), 308, (315), 323 mμ [log ε (4·70), 4·90, (3·02), 3·78, 3·81, (3·69), 2·95, (2·73), 2·77]. The infrared spectrum was identical with that of authentic material, and the picrate formed orange needles, m. p. and mixed m. p. 106—108°.

Attempted Isomerisation of 4-*Acetylnaphthothiophen.*—Aluminium chloride (100 mg.) was added to a solution of 4-acetylnaphthothiophen (117 mg.) in nitrobenzene (1·5 ml.). After 18 hr. the deep red solution was decomposed with ice and nitrobenzene removed with steam. Analysis of the recovered (in benzene) neutral gum (117 mg.) by vapour-phase chromatography showed less than 1% of isomerisation to 3-acetyl compound.

Acetylation in methylene chloride (3 ml.) with naphthothiophen (50 mg.), aluminium

[22] Brown and Hammick, *J.*, 1948, 1395.

chloride (45 mg.), and acetyl chloride (0·035 ml.), and analysis of the neutral product obtained after 1 hr. and 24 hr. by vapour-phase chromatography gave ratios of the 3- and the 4-isomer of 0·41 : 1 and 0·43 : 1.

I thank Mr. A. G. Douglas for some preliminary experiments.

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