2-(2-Naphthyl)benzo[*b*]thiophen. Part II.[1] Halides, and the Keto-sulphone

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The preparation and some of the reactions of 3-halogeno-2-(2-naphthyl)benzo[*b*]thiophens and their corresponding sulphones, and the tautomeric keto-sulphone 2,3-dihydro-2-(2-naphthyl)-3-oxobenzo[*b*]thiophen 1,1-dioxide, are described. Methods, involving sulphonation or halogenation, of separating 2-(2-naphthyl)benzo[*b*]thiophen from 2,2′-binaphthyl are briefly described.

2-(2-NAPHTHYL)BENZO[*b*]THIOPHEN (I; R = H) was first prepared synthetically by Murthy and Tilak,[2] but a more convenient source is from crude coal-tar naphthalene by heating with fuller's earth.[3]

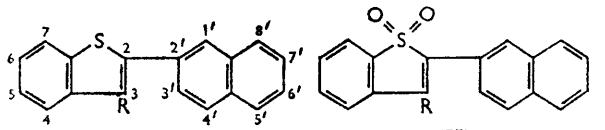
Chlorination and iodination, like bromination,[1] gave the 3-monohalogeno-compounds (I; R = Hal). The structure of the new halides has been proved by conversion, through the sulphones (II; R = Cl or I), into 2-(2-naphthyl)-3-piperidinobenzo[*b*]thiophen 1,1-dioxide (II; R = NC_5H_{10}), identical with material similarly prepared from the known 3-monobromide. All three halogeno-naphthylbenzo[*b*]thiophens (I; R = Cl, Br, or I) were reduced to the parent heterocycle in good yields by heating with concentrated hydriodic acid, but were unchanged by attempted catalytic (palladium–charcoal) hydrogenation at room temperature and pressure. The iodide (but not the bromide or chloride) could also be reduced by tin and hydrochloric acid; and the bromide (others not tested) could be reduced by way of its Grignard reagent.

The 3-halogeno-1,1-dioxides (II; R = Cl, Br, or I) are formally extended sulphonyl halides and might be expected, particularly by analogy with corresponding compounds in the benzo[*b*]thiophen series,[4] to be much more reactive than the unoxidised sulphides towards nucleophilic reagents. The piperidino-, morpholino-,

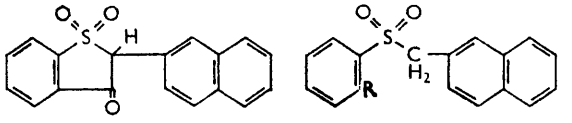
[1] Part I, A. H. Lamberton and P. T. McGrail, *J. Chem. Soc.*, 1963, 1776.
[2] T. S. Murthy and B. D. Tilak, *J. Sci. Ind. Res., India*, 1960, **19***B*, 395.
[3] A. H. Lamberton and P. T. McGrail, *Chem. and Ind.*, 1961, 986.
[4] F. G. Bordwell and C. J. Albisetti, *J. Amer. Chem. Soc.*, 1948, **70**, 1558; G. Komppa, *J. prakt. Chem.*, 1929, **122**, 319.

methoxy-, ethoxy-, and thiophenoxy-derivatives were easily prepared but, unexpectedly, we failed to induce reactions with aniline or diethylamine.

Hydrolysis of either the piperidino- or morpholino-1,1-dioxide by heating with dilute sulphuric acid gave



(I) (II)

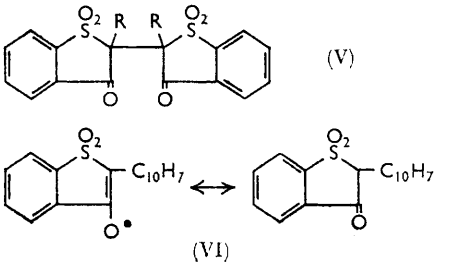


(III) (IV)

material which we formulate as the keto-sulphone 2,3-dihydro-2-(2-naphthyl)-3-oxobenzo[*b*]thiophen 1,1-dioxide (III) on grounds of spectroscopy and oximation, as well as by analogy.[5] The keto-sulphone dissolved easily in aqueous alkalis to give a yellow solution presumably containing the enolate anion (II; R = O^-), and was regenerated on acidification. Heating the keto-sulphone with aqueous sodium hydroxide yielded (on acidification, and similarly to the benzo[*b*]thiophen series [6]) *o*-(2-naphthylmethylsulphonyl)benzoic acid (IV; R = CO_2H). This acid was decarboxylated to give the sulphone (IV; R = H), whose structure was proved by reduction to benzenesulphinic acid and 2-methylnaphthalene, and by synthesis from sodium benzenesulphinate and 2-bromomethylnaphthalene. The completed degradation provides an additional proof of the structure of the initial material (I; R = H), and of the preferred position (3) of electrophilic substitution.

Treatment of the keto-sulphone (III) with diazomethane gave the *O*-methyl derivative (II; R = OMe), identical with material prepared from the monobromide (II; R = Br) by the action of potassium methoxide. As in the benzo[*b*]thiophen series,[7] hydrolysis with acid regenerated the keto-sulphone, whilst alkali led to the acid (IV; R = CO_2H), already obtained directly from (III). On the assumption that any *C*-methyl derivative formed would remain unattacked, we sought to find it after destructive alkaline hydrolysis of the *O*-methyl compound in the crude methylation product—but without success.

The keto-sulphone (III) reacted with bromine to give mainly the bi-benzo[*b*]thienyl compound (V; R = 2-naphthyl), which could be obtained in a pure condition more readily by the action of potassium ferricyanide in alkaline solution, and presumably arose by dimerisation of the radical (VI). Cohen and Smiles [8] reported substitutive bromination of the corresponding keto-sulphone with phenyl in place of the 2-naphthyl group, and, though oxidative dimerisation is common in the sulphide series [*e.g.*, formation of thio-indigo white [9] (V; R = Ph and S for SO_2)], we are not aware of any previous cases involving the closely related sulphones. A Diels–Alder type dimerisation, postulated [10] as the first step in a reaction of benzo[*b*]thiophen 1,1-dioxide, seems most unlikely in our conditions of preparation. Since the



(V)

(VI)

sulphone rings are not aromatic, the molecule (V; R = 2-naphthyl) is less sterically congested than might appear at first sight.

EXPERIMENTAL

Room temperature was 20° ± 3°. Infrared spectra were determined on a Perkin-Elmer Infracord model 127. In certain obvious cases ' ether extraction ' implies subsequent drying and evaporation, either at once or after washing as specified in the text.

Chlorination and Iodination.—2-(2-Naphthyl)benzo[*b*]-thiophen (2·6 g.) was stirred until dissolved (1 hr. at room temperature) in a solution of chlorine (0·75 g.) in carbon tetrachloride (50 ml.). The solvent was removed under reduced pressure and the residue crystallised from ethanol to give *3-chloro-2-(2-naphthyl)benzo*[b]*thiophen* (2·7 g.) as a micro-crystalline powder, m. p. 95° (Found: C, 73·8; H, 3·9; Cl, 11·8. $C_{18}H_{11}ClS$ requires C, 73·7; H, 3·8; Cl, 12·0%). Mercuric oxide (4 g.) and iodine (5 g.) were added, alternately and portionwise in 2 hr., to a refluxing mixture of 2-(2-naphthyl)benzo[*b*]thiophen (4·4 g.) in n-hexane (25 ml.). After a further 12 hr. refluxing, the iodine coloration had almost disappeared; the mixture was then cooled, carbon tetrachloride (50 ml.) added, and the undissolved material collected. The filtrate was washed with sodium hydrogen sulphite solution and water, dried, and evaporated; the residue yielded *3-iodo-2-(2-naphthyl)benzo*[b]-*thiophen* (2·45 g.) as a micro-crystalline powder, m. p. 92—93° (from ethanol) (Found: C, 56·0; H, 2·7; I, 32·8. $C_{18}H_{11}IS$ requires C, 56·3; H, 2·4; I, 33·0%).

Reduction of the Halogeno-compounds.—3-Chloro-, 3-bromo-, or 3-iodo-2-(2-naphthyl)benzo[*b*]thiophen (0·002 mole) was refluxed for 1 hr. with constant-boiling hydriodic acid (5 ml.). The mixture was poured into water (20 ml.), and the precipitate crystallised from carbon tetrachloride

[5] H. D. Hartough and S. L. Meisel, ' Compounds with Condensed Thiophene Rings,' Interscience, New York, 1954, pp. 64 and 157.
[6] F. Arndt, A. Kirsch, and P. Nachtwey, *Ber.*, 1926, **59**, 1074.
[7] F. Arndt and C. Martius, *Annalen*, 1932, **499**, 228.
[8] A. Cohen and S. Smiles, *J. Chem. Soc.*, 1930, 406.
[9] L. Kalb and J. Bayer, *Ber.*, 1913, **46**, 3879.
[10] F. G. Bordwell, W. H. McKellin, and D. Babcock, *J. Amer. Chem. Soc.*, 1951, **73**, 5566.

to give 2-(2-naphthyl)benzo[*b*]thiophen, m. p. 211—212°; yields 71, 86, and 83%, respectively.

The Grignard reagent from the 3-bromo-compound (5 g.) (prepared in tetrahydrofuran as described,[1] including the refluxing period of 1 hr.) was poured on to solid ammonium chloride (3 g.). After 1 hr., excess of 2N-hydrochloric acid was added, with cooling, and the aqueous layer separated. Carbon tetrachloride (150 ml.) was added to the residual layer and, after washing with water, drying, and evaporation, the residue yielded 2-(2-naphthyl)benzo[*b*]thiophen (2·35 g.), m. p. 211—212° (from carbon tetrachloride).

3-Iodo-2-(2-naphthyl)benzo[*b*]thiophen (0·5 g.) was refluxed for 3 hr. with granulated tin (1 g.) and conc. hydrochloric acid (5 ml.) in ethanol (15 ml.). The cooled mixture was extracted with carbon tetrachloride (2 × 40 ml.) and the extracts, after washing with sodium hydroxide and with water, drying, and evaporation, yielded 2-(2-naphthyl)-benzo[*b*]thiophen (0·15 g.), m. p. 211—212° (from carbon tetrachloride). The chloro- and bromo-compounds were recovered, even after heating for 24 hr. under the same conditions.

No hydrogen was taken up, and the initial material thereafter recovered, when any of the three halogeno-compounds was stirred in acetic acid solution for 24 hr. with a 10% palladium–charcoal catalyst in an atmosphere of hydrogen at room temperature and pressure.

Preparation of the Halogeno-sulphones.—3-Chloro-2-(2-naphthyl)benzo[*b*]thiophen (1 g.) was refluxed for 1 hr. with glacial acetic acid (10 ml.), acetic anhydride (2·5 ml.), and hydrogen peroxide (30%; 2·5 ml.). The yellow solution was cooled in ice, and the resultant precipitate recrystallised from acetic acid to yield *3-chloro-2-(2-naphthyl)benzo*[b]*thiophen 1,1-dioxide* (0·7 g.) as pale yellow felted needles, m. p. 152—153°, $\nu_{max.}$ (KBr) 1300 and 1160 (sulphone) cm.$^{-1}$ (Found: C, 65·9; H, 3·8; Cl, 10·8. $C_{18}H_{11}ClO_2S$ requires C, 66·0; H, 3·4; Cl, 10·6%). Similar treatment of the iodide (0·5 g.), using hydrogen peroxide (30%; 1·3 ml.) and acetic acid (7 ml.), but no anhydride, gave *3-iodo-2-(2-naphthyl)benzo*[b]*thiophen 1,1-dioxide* (0·15 g.) as pale yellow needles, m. p. 187—188° (from acetic acid), $\nu_{max.}$ (KBr) 1280 and 1150 (sulphone) cm.$^{-1}$ (Found: C, 50·4; H, 2·6; I, 30·0; S, 7·9. $C_{18}H_{11}IO_2S$ requires C, 51·7; H, 2·7; I, 30·3; S, 7·7%). The purity of the material might be questioned on the ground of the carbon analysis, but this would not invalidate the proof of iodination in the 3-position. The bromo-sulphone has already [1] been described.

Piperidino- and Morpholino-sulphones.—The chloro-, bromo-, or iodo-2-(2-naphthyl)benzo[*b*]thiophen 1,1-dioxide (0·3, 0·5, or 0·23 g., respectively) was refluxed for 1 hr. with piperidine (0·8, 0·35, or 0·9 g.) in ethanol (25, 20, or 8 ml.). The solid which separated on cooling in ice was crystallised from moist acetone to yield identical (mixed m. p. and i.r. spectrum) specimens of *2-(2-naphthyl)-3-piperidinobenzo*[b]*thiophen 1,1-dioxide* (0·24, 0·42, or 0·07 g.) as yellow needles, m. p. 233—235° (Found: C, 73·3; H, 5·7. $C_{23}H_{21}NO_2S$ requires C, 73·6; H, 5·6%). 3-Chloro-2-(2-naphthyl)benzo-[*b*]thiophen 1,1-dioxide (0·3 g.) was refluxed overnight with morpholine (0·4 ml.) in ethanol (10 ml.); cooling, collection and crystallisation from ethanol gave *3-morpholino-2-(2-naphthyl)benzo*[b]*thiophen 1,1-dioxide* (0·24 g.) as yellow needles, m. p. 244—246°, $\nu_{max.}$ (KBr) 1290 and 1150 (sulphone) cm.$^{-1}$ (Found: C, 70·1; H, 5·3. $C_{22}H_{19}NO_3S$ requires C, 70·1; H, 5·1%), which could be obtained similarly in almost identical yield from the bromo-sulphone.

Methoxy-, Ethoxy-, and Thiophenoxy-sulphones.— 3-Bromo-2-(2-naphthyl)benzo[*b*]thiophen 1,1-dioxide (0·75 g.) was refluxed for ½ hr. with potassium hydroxide (0·12 g.) in dry methanol (20 ml.). The product was worked up by water dilution, ether extraction, and crystallisation from methanol (charcoal) to yield the methoxy-compound (0·23 g.), m. p. 131—132°, identical (mixed m. p. and i.r. spectrum) with material prepared by the action of diazomethane on the keto-sulphone (*q.v.* for analysis). Similar, though not identical, treatment using dry ethanol gave on evaporation a gum, which was dissolved in chloroform and purified by passage down a silica column; evaporation and crystallisation from ethanol gave *3-ethoxy-2-(2-naphthyl)benzo*[b]*thiophen 1,1-dioxide* (0·21 g. from 0·37 g. of the bromide) as pale yellow needles, m. p. 106—107° (Found: C, 71·2; H, 5·1; S, 9·8. $C_{20}H_{16}O_3S$ requires C, 71·4; H, 4·8; S, 9·5%).

3-Bromo-2-(2-naphthyl)benzo[*b*]thiophen 1,1-dioxide (0·37 g.) was refluxed overnight with thiophenol (0·11 ml.) and potassium hydroxide (0·063 g.) in dry ethanol (20 ml.). After dilution with water and extraction with ether (washed with dil. sodium hydroxide and with water), crystallisation from methanol yielded *2-(2-naphthyl)-3-thiophenoxybenzo*[b]*thiophen 1,1-dioxide* (0·15 g.) as brown needles, m. p. 139—140° (Found: S, 16·0. $C_{24}H_{16}O_2S_2$ requires S, 16·0%).

Preparation of the Keto-sulphone (III).—2-(2-Naphthyl)-3-piperidinobenzo[*b*]thiophen 1,1-dioxide (3 g.) was refluxed for 6 hr. with sulphuric acid (10% v/v; 200 ml.). After cooling, the insoluble material was collected, washed with water, dried, and crystallised from acetone to yield *2,3-dihydro-2-(2-naphthyl)-3-oxobenzo*[b]*thiophen 1,1-dioxide* (2·1 g.) as needles, m. p. 186—187°, $\nu_{max.}$ (KBr) 1740 (carbonyl), and 1310 and 1160 (sulphone) cm.$^{-1}$ (Found: C, 69·8; H, 4·2. $C_{18}H_{12}O_3S$ requires C, 70·1; H, 3·9%); easily soluble in aqueous sodium hydroxide or hydrogen carbonate at room temperature, and regenerated on acidification. One later sample was found to contain traces of the initial piperidino-compound, and purification by way of the soluble sodium enolate might be advantageous. The morpholino-sulphone gave an identical yield of (III) on similar treatment. The *oxime* of 2,3-dihydro-2-(2-naphthyl)-3-oxobenzo[*b*]thiophen 1,1-dioxide was prepared, by refluxing overnight with hydroxylamine hydrochloride in methanol buffered with sodium acetate, as needles, m. p. 240—242° (from ethanol) (Found: C, 67·1; H, 4·3. $C_{18}H_{13}NO_3S$ requires C, 66·9; H, 4·1%).

Degradation of the Keto-sulphone.—2,3-Dihydro-2-(2-naphthyl)-3-oxobenzo[*b*]thiophen 1,1-dioxide (0·30 g.) was refluxed for 4 hr. in aqueous sodium hydroxide (20%; 7 ml.). After acidification and ether extraction, the acid products were separated ($NaHCO_3$) and ether extraction of the acidified hydrogen carbonate washings gave material which was crystallised from aqueous ethanol to yield *o-(2-naphthylmethylsulphonyl)benzoic acid* (0·26 g.) as platelets, m. p. 169—170°, $\nu_{max.}$ (KBr) 1700 (carboxy CO), and 1310 and 1150 (sulphone) cm.$^{-1}$ (Found: C, 66·1; H, 4·6. $C_{18}H_{14}O_4S$ requires C, 66·3; H, 4·3%).

The above-mentioned sulphonylbenzoic acid (0·18 g.) was refluxed for ½ hr. with copper powder (0·18 g.) in quinoline (4 ml.). After cooling and removal of copper, the filtrate was acidified and the resultant precipitate collected to yield, on crystallisation from ether–ethanol (1 : 1), *2-naphthylmethyl phenyl sulphone* (0·08 g.) as lustrous plates, m. p. 186—187°, $\nu_{max.}$ (KBr) 1300 and 1150 (sulphone) cm.$^{-1}$ (Found: C, 72·2; H, 5·3. $C_{17}H_{14}O_2S$ requires C, 72·1; H, 5·0%), identical with synthetic material.

In addition, a sample of 2-naphthylmethyl phenyl sulphone (0·5 g.) was reduced by refluxing for 4 hr. with sodium amalgam (6%; 13 g.) and dry ethanol (15 ml.). Filtration, acidification, and ether extraction gave 2-methylnaphthalene (0·12 g.), m. p. 33—34°, identified by mixed m. p. and i.r. spectrum; the sulphinic acid in the aqueous layers was identified by neutralisation (NaOH) and evaporation, followed by refluxing the residue with benzyl chloride (1 ml.) in ethanol (10 ml.) for 6 hr., when, on pouring into water (30 ml.) benzyl phenyl sulphone (0·18 g.), m. p. 147—148°, identified by mixed m. p. and i.r. spectrum, was produced.

Synthesis of 2-Naphthylmethyl Phenyl Sulphone.—2-Bromomethylnaphthalene [11] (24 g.) was refluxed for 6 hr. with sodium benzenesulphinate dihydrate (22 g.) in ethanol (100 ml.). After pouring into water (300 ml.) the precipitate was collected, washed with water and with ethanol, and crystallised from ethanol to yield the sulphone (9·0 g.), m. p. 186—187°, identical (mixed m. p. and i.r. spectrum) with material prepared by degradation from the keto-sulphone (III).

Action of Diazomethane on the Keto-sulphone.—2,3-Dihydro-2-(2-naphthyl)-3-oxobenzo[*b*]thiophen 1,1-dioxide (0·31 g.) in tetrahydrofuran (*ca.* 5 ml.) was treated with an excess of diazomethane in ether. After setting aside for 24 hr., evaporation gave a crude methylation product (0·32 g.) which yielded 3-*methoxy*-2-(2-*naphthyl*)*benzo*[b]-*thiophen* 1,1-*dioxide* (0·17 g.) as pale yellow needles, m. p. 131—132°, on crystallisation from methanol (charcoal), identical with material prepared from the 3-bromo-sulphone by the action of potassium methoxide; $\nu_{max.}$ (KBr) 1290 and 1160 (sulphone) cm.$^{-1}$, no carbonyl absorption (Found: S, 9·9. $C_{19}H_{14}O_3S$ requires S, 9·8%). Refluxing the 3-methoxy-sulphone (0·12 g.) with conc. hydrochloric acid (2 ml.) for 1 hr. regenerated the keto-sulphone, m. p. 186—187°, in almost quantitative yield.

The 3-methoxy-sulphone (60 mg.) was refluxed for 5 hr. with aqueous potassium hydroxide (20%; 5 ml.)., and the product worked up by acidification, ether extraction, and separation ($NaHCO_3$) of the acid products. Ether extraction of the acidified hydrogen carbonate washings yielded impure *o*-(2-naphthylmethylsulphonyl)benzoic acid (46 mg.), m. p. 165—167°, but identical (mixed m. p. and i.r. spectrum) with material prepared directly from the keto-sulphone.

In another experiment an ethereal solution of the crude methylation product (initial keto-sulphone absent by test of $NaHCO_3$ extraction and acidification) was divided into two portions. One portion was worked up, as a check, to yield the methoxy-sulphone. The other (from 0·61 g. of the keto-sulphone) was evaporated and the residue refluxed for 5 hr. with potassium hydroxide (2 g.) in water (10 ml.). On working up, the sulphonyl benzoic acid was isolated as before; the neutral material—assumed to contain any C-methylation product, if the latter were stable to alkali—was only 20 mg.; and was identified, after crystallisation from ether, as at least mainly (12 mg.) the piperidino-compound (II; R = NC_5H_{10}), of which traces must have been present in the initial keto-sulphone.

Oxidative Dimerisation of the Keto-sulphone.—2,3-Dihydro-2-(2-naphthyl)-3-oxobenzo[*b*]thiophen 1,1-dioxide (1 g.) was dissolved in aqueous sodium hydrogen carbonate (250 ml.) and ethanol (100 ml.), and heated on the steam-bath for 3 hr. with potassium ferricyanide (4 g. in 40 ml. of water). The resultant precipitate was collected and dissolved in benzene; after washing with sodium hydrogen carbonate, drying, and evaporation, the residue was crystallised from ethanol (charcoal) to yield 2,2′,3,3′-*tetrahydro*-2,2′-*di*-(2-*naphthyl*)-3,3′-*dioxo*-2,2′-*bi*(*benzo*[b]-*thienyl*) 1,1,1′,1′-*tetraoxide* (V; R = 2-naphthyl) (0·33 g.) as a microcrystalline powder, m. p. 228—230° (Found: C, 69·9; H, 3·7; S, 10·5%; *M*, 610. $C_{36}H_{22}O_6S_2$ requires C, 70·3; H, 3·8; S, 10·4%; *M*, 615). The material did not dissolve in cold aqueous sodium hydroxide or hydrogen carbonate, and was recovered after refluxing for 6 hr. with 20% aqueous sodium hydroxide. Reaction of the keto-sulphone (0·10 g.) with bromine (0·06 ml.) in acetic acid (22 ml.) led to fading of the coloration in ½ hr. at 50° but, on working up, the product (54 mg.), m. p. 212—214° (from ethanol), contained little bromine (Found: Br, 3·2%) and was mainly the dimer on the evidence of the mixed m. p. and i.r. spectrum.

Chemical Separation of 2-(2-Naphthyl)benzo[b]*thiophen and 2,2′-Binaphthyl.*—Preparation of the first of these gives, as a by-product, some intermediate vacuum distillation fractions which are mixtures of the pair, in proportions which make separation by crystallisation difficult. Pure 2-(2-naphthyl)-benzo[*b*]thiophen (10·00 g.) was stirred for 1 hr. at room temperature with conc. sulphuric acid (26·00 g.); collection of the undissolved material (5·21 g.) and acidimetry showed that, on average, between 3 and 3½ sulphonate groups had been introduced. The initial material was regenerated on dilution with water and heating to 150—160° for 24 hr. When a mixture (6 g.; *ca.* 35% of the thiophen by S analysis) was stirred at room temperature for 5 hr. with sulphuric acid (96%; 25 ml.), the 2-(2-naphthyl)benzo-[*b*]thiophen was preferentially sulphonated; addition to water gave 2,2′-binaphthyl (3·5 g.), whilst heating a portion of the filtrate with additional water gave 2-(2-naphthyl)-benzo[*b*]thiophen in yield corresponding to a total recovery of 1·6 g.

A more convenient separation was by preferential halogenation. A mixture (20 g.; *ca.* 35 : 65 as before) was stirred with chlorine (3·25 g.) in carbon tetrachloride (110 ml.) for ½ hr. at room temperature. The undissolved 2,2′-binaphthyl was collected (12 g.), m. p. 182—183°, and a further small crop (0·6 g.) obtained by concentration of the filtrate to 60 ml., and setting aside for 2 hr. Evaporation of the second filtrate yielded almost pure 3-chloro-2-(2-naphthyl)benzo[*b*]thiophen (7·3 g.), m. p. 93° (from ethanol) (Found: C, 73·9; H, 4·0; Cl, 11·8. Calc. for $C_{18}H_{11}ClS$: C, 73·7; H, 3·8; Cl, 12·0%). Preferential bromination could be used in similar fashion, but attempts to mercurate 2-(2-naphthyl)benzo[*b*]thiophen (method of Challenger and Miller [12]) were unsuccessful.

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[11] N. B. Chapman and J. F. A. Williams, *J. Chem. Soc.*, 1952, 5044.

[12] F. Challenger and S. A. Miller, *J. Chem. Soc.*, 1939, 1005.