2-(2-Naphthyl)benzo[*b*]thiophen. Part III.[1] Compounds Derived from Nitration of the Halogeno-derivatives

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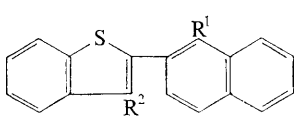
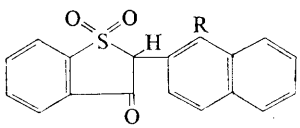
The preparation and some reactions of 3-chloro- and 3-bromo-2-(1-nitro-2-naphthyl)benzo[*b*]thiophens are described.

NITRATION of 3-chloro- and 3-bromo-2-(2-naphthyl)-benzo[*b*]thiophens gave the 3-halogeno-2-(1-nitro-2-naphthyl)benzo[*b*]thiophens (I; $R^1 = NO_2$, R^2 = Cl or Br). The position of nitration was proved by the reduction of the bromo-compound with Raney nickel to 1-amino-2-phenethylnaphthalene ($PhCH_2{\cdot}CH_2{\cdot}C_{10}H_6{\cdot}NH_2$), which was identified by comparison with synthetic material. Milder reduction gave the 3-halogeno-2-(1-amino-2-naphthyl)benzo[*b*]thiophens (I; $R^1 = NH_2$, R^2 = Cl or Br).



(I)



(II)

The position of nitration was shown to be identical in the two halogeno-nitro-compounds by oxidation to the corresponding sulphones, followed by conversion into the same piperidino-derivative (I; $R^1 = NO_2$, $R^2 = NC_5H_{10}$, SO_2 for S). The series of conversions (halide into halogeno-sulphone, piperidino-sulphone, and finally keto-sulphone) has been recently described [1] for the corresponding compounds without the nitro-group, but the sulphone ring of the nitro-keto-sulphone (II; R = NO_2) could not be opened smoothly as was the case [1] for (II; R = H). We therefore found an alternative method for proof of structure in the use of Raney nickel (see above), though oxidative degradation of the nitro-keto-sulphone gave us the first hint of the position of nitration.

The preparation of derivatives such as the *O*-methyl ether of the nitro-keto-sulphone and the synthesis of 1-amino-2-phenethylnaphthalene are dealt with in the Experimental section.

EXPERIMENTAL

Room temperature was 20 ± 3°. I.r. spectra were determined with a Perkin-Elmer Infracord model 127, and n.m.r. spectra with a Varian A 60 spectrometer. Materials recorded as identical were proved to be so by m.p., mixed m.p., and the comparison of i.r. spectra.

Nitration of the Halides.—Fuming nitric acid (0·65 ml.) in acetic acid (5 ml.) was added dropwise during 0·5 hr. to 3-chloro- or 3-bromo-2-(2-naphthyl)benzo[*b*]thiophen (3·0 or 3·4 g., respectively) in acetic acid (25 ml.) stirred and heated on a steam bath. The mixture was heated for a further 0·5 hr. and cooled; the precipitate gave pale yellow needles of *3-chloro-2-(1-nitro-2-naphthyl)benzo*[b]*thiophen* (1·3 g.), m.p. 193—194° (from acetic acid) (Found: C, 63·8; H, 3·4; Cl, 10·6. $C_{18}H_{10}ClNO_2S$ requires C, 63·6; H, 3·0; Cl, 10·4%) or of *3-bromo-2-(1-nitro-2-naphthyl)-benzo*[b]*thiophen* (1·7 g.), m.p. 192—193° (from acetic acid), $\nu_{max.}$ (KBr) 1520 (NO_2) cm.$^{-1}$ (Found: C, 56·4; H, 2·7; Br, 20·6. $C_{18}H_{10}BrNO_2S$ requires C, 56·2; H, 2·6; Br, 20·8%).

Oxidation to the Sulphones.—Oxidation of the nitrohalides with hydrogen peroxide–acetic acid–acetic anhydride (essentially as in ref. 1) gave yellow needles of *3-chloro-2-(1-nitro-2-naphthyl)benzo*[b]*thiophen 1,1-dioxide* (71%), m.p. 219—220° (from acetic acid) (Found: C, 57·9; H, 3·0; Cl, 9·5. $C_{18}H_{10}ClNO_4S$ requires C, 58·2; H, 2·7; Cl, 9·6%) or of *3-bromo-2-(1-nitro-2-naphthyl)benzo*[b]*thiophen 1,1-dioxide* (67%), m.p. 241—242° (from acetic acid), $\nu_{max.}$ (KBr) 1520, 1300, and 1160 (NO_2 and SO_2) cm.$^{-1}$ (Found: C, 52·1; H, 2·7; Br, 18·9. $C_{18}H_{10}BrNO_4S$ requires C, 51·9; H, 2·4; Br, 19·2%).

The Piperidino-derivative (I; $R^1 = NO_2$, $R^2 = NC_5H_{10}$, SO_2 *for* S) *and the Nitro-keto-sulphone* (II; R = NO_2).—3-Chloro-2-(1-nitro-2-naphthyl)benzo[*b*]thiophen 1,1-dioxide (2·4 g.) was heated under reflux for 2 hr. with piperidine (2 ml.) in ethanol (80 ml.) and then cooled. The product was collected, and gave golden rhombs of *3-piperidino-2-(1-nitro-2-naphthyl)benzo*[b]*thiophen 1,1-dioxide* (2·25 g.), m.p. 252—253° (from acetone), $\nu_{max.}$ (KBr) 1520, 1290, and 1150 (NO_2 and SO_2) cm.$^{-1}$ (Found: C, 65·5; H, 4·7. $C_{23}H_{20}N_2O_4S$ requires C, 65·7; H, 4·8%). Similar treatment of the bromide gave identical material.

3-Piperidino-2-(1-nitro-2-naphthyl)benzo[*b*]thiophen 1,1-dioxide (0·21 g.) was heated under reflux with aqueous sulphuric acid (30% v/v; 25 ml.) for 7 hr. The mixture

[1] Part II, A. H. Lamberton and J. E. Thorpe, *J. Chem. Soc.* (*C*), 1967, 2571.

was cooled and the precipitate was collected, washed with water, and dried; it gave pale yellow needles of *2,3-dihydro-2-(1-nitro-2-naphthyl)-3-oxobenzo*[b]*thiophen* 1,1-*dioxide* (0·13 g.), m.p. 222—223° (from acetone), $\nu_{max.}$ (KBr) 1730 (C=O), 1520, 1310, and 1180 (NO_2 and SO_2) cm.$^{-1}$ (Found: C, 61·0; H, 3·4. $C_{18}H_{11}NO_5S$ requires C, 61·2; H, 3·1%). This material dissolved readily in 2N-sodium hydroxide, or in aqueous sodium hydrogen carbonate, to give a clear orange solution, from which it was regenerated by acidification.

Degradation of the Nitro-keto-sulphone.—The production of some phthalic acid and *o*-sulphobenzaldehyde (after alkaline oxidation with potassium permanganate and potassium hydroxide in water) suggested that the nitro-group was in position 1 (II; R = NO_2) 2, or 3 of the naphthalene ring. Oxidation with chromium trioxide in moist acetic acid was ineffective. Attempts to open the sulphone ring by heating with aqueous potassium hydroxide [1] gave acidic material which contained no sulphonyl group (i.r. spectrum) and was not further investigated.

The O-Methyl Ether of the Nitro-keto-sulphone (I; R^1 = NO_2, R^2 = OMe, SO_2 for S).—(*a*) A solution of 2,3-dihydro-2-(1-nitro-2-naphthyl)-3-oxobenzo[*b*]thiophen 1,1-dioxide (0·71 g.) in tetrahydrofuran (150 ml.) was cooled to 0°, treated with an excess of ethereal diazo-methane, and set aside overnight. Evaporation then left material which was chromatographed on silica with chloroform as eluant and gave pale yellow needles of *3-methoxy-2-(1-nitro-2-naphthyl)benzo*[b]*thiophen* 1,1-*dioxide* (0·46 g.), m.p. 229—231° (from acetone) (Found: C, 62·3; H, 3·8; N, 4·0. $C_{19}H_{13}NO_5S$ requires C, 62·1; H, 3·6; N, 3·8%).

(*b*) 3-Bromo-2-(1-nitro-2-naphthyl)benzo[*b*]thiophen 1,1-dioxide (200 mg.) was heated under reflux for 2 hr. with potassium hydroxide (33 mg.) in dry methanol (10 ml.). The mixture was evaporated and the residue dissolved in benzene; the solution was washed with dilute sodium hydroxide, the benzene was evaporated off, and the residue was crystallised from acetone (charcoal) to yield material (112 mg.) identical with that obtained from the nitro-keto-sulphone.

Reduction of the Halogeno-nitro-compounds.—(*a*) A suspension of 3-bromo-2-(1-nitro-2-naphthyl)benzo[*b*]thiophen (0·75 g.) in acetic acid (50 ml.) was hydrogenated for 8 hr. at room temperature and pressure, over palladium–charcoal. The solution was filtered and evaporated to dryness and the residue gave pale brown needles of *3-bromo-2-(1-amino-2-naphthyl)benzo*[b]*thiophen* (0·1 g.), m.p. 159—160° [from methanol (charcoal)] (Found: C, 60·7; H, 4·0; N, 4·1. $C_{18}H_{12}BrNS$ requires C, 61·0; H, 3·4; N, 4·0%). Similar treatment of the chloride (0·17 g.) gave *3-chloro-2-(1-amino-2-naphthyl)benzo*[b]*thiophen* (0·05 g.) as pale brown needles, m.p. 196—198° (from ethanol) (Found: C, 69·8; H, 4·1. $C_{18}H_{12}ClNS$ requires C, 69·8; H, 3·9%). When heated with acetic anhydride in acetic acid the bromo-amine gave *3-bromo-2-(1-acetamido-2-naphthyl)benzo*[b]*thiophen* as needles, m.p. 209—210° (from acetone) (Found: C, 60·1; H, 3·8. $C_{20}H_{14}BrNOS$ requires C, 60·6; H, 3·5%).

(*b*) 3-Bromo-2-(1-nitro-2-naphthyl)benzo[*b*]thiophen (0·38 g.) was heated under reflux for exactly 55 min. with Raney nickel (type W-2; [2] 6 g.) in ethanol (30 ml.). The mixture was filtered and evaporated to leave a brown solid (0·25 g.) which was chromatographed on silica with benzene as eluant. The earlier fractions contained three products, but material from later fractions was homogeneous (t.l.c.). The residue from evaporation of the later fractions was dissolved in ether. The solution was filtered and evaporated to give pale brown cubes of *1-amino-2-phenethylnaphthalene* (0·12 g.), m.p. 72—73°, identified by comparison with synthetic material (Found: C, 88·4; H, 5·6; N, 5·4. $C_{18}H_{17}N$ requires C, 88·5; H, 5·8; N, 5·7%), τ ($CDCl_3$) 2·2—2·9 (aromatic), 6·25br (NH_2), and 7·17 (s, CH_2), cf. 2-phenethylnaphthalene: [3] τ 2·1—2·9 and 6·95(s). When the amine was heated with acetic anhydride in acetic acid it gave *1-acetamido-2-phenethylnaphthalene* as needles, m.p. 157—158° (from benzene–light petroleum), $\nu_{max.}$ 3300 and 1650 (RNH·CO and CO) cm.$^{-1}$ (Found: C, 82·9; H, 7·0; N, 4·6. $C_{20}H_{19}NO$ requires C, 83·0; H, 6·6; N, 4·8%).

Synthesis of 1-Amino- and 1-Acetamido-2-phenethylnaphthalenes.—1-Nitro-2-naphthylpyruvic acic was prepared from 2-methylnaphthalene by nitration [4] and a condensation with ethyl oxalate.[5] Potassium permanganate (3 g.) in water (50 ml.) was added during 2 min. to a well stirred and ice-cooled mixture of 1-nitro-2-naphthylpyruvic acid (5 g.), sodium hydroxide (1·6 g.), toluene (400 ml.), and water (100 ml.). After 5 min. the toluene was separated and evaporated to leave ether-soluble material (*ca.* 1 g.); crystallisation of this from light petroleum (b.p. 60—80°) yielded 1-nitro-2-naphthaldehyde, m.p. 101° (lit.,[6] 99°), $\nu_{max.}$ (KBr) 1700 (C=O) cm.$^{-1}$, τ −0·15 (CHO).

A solution of 1-nitro-2-naphthaldehyde (1 g.) in dry ethanol (100 ml.) was added dropwise, with stirring and under an atmosphere of nitrogen, to a Wittig reagent prepared from dry ethanol (120 ml.), sodium (0·4 g.), and triphenylbenzylphosphonium chloride (4 g.). After 1 hr. the liquid was evaporated to a small bulk, and *trans-1-nitro-2-styrylnaphthalene* (0·5 g.) was collected. It gave yellow needles, m.p. 150° (from ethanol), $\nu_{max.}$ (KBr) 1520 (NO_2), 965 (*trans* CH=CH), and 730 and 690 (Ph) cm.$^{-1}$ [Found: C, 78·2; H, 4·4%; M^+ (mass spectrum), 275. $C_{18}H_{13}NO_2$ requires C, 78·5; H, 4·8%; *M*, 275]. We consider the compound to be the *trans*-isomer since (*a*) the sharp i.r. absorption at 965 cm.$^{-1}$ was removed by hydrogenation, though the bands at 730 and 690 cm.$^{-1}$ were only slightly changed (to 725 and 695 cm.$^{-1}$ in 1-amino-2-phenethylnaphthalene), and (*b*) the n.m.r. signals lay wholly in the aromatic region [τ ($CDCl_3$) 2·05—2·80; cf. olefinic proton signals at τ 3·45 and 2·90 in the spectra of *cis*- and *trans*-stilbene, respectively [7]].

trans-1-Nitro-2-styrylnaphthalene was also prepared by the Meerwein reaction of cinnamic acid with diazotised 1-nitro-2-naphthylamine, but the yield (*ca.* 1% after isolation by t.l.c.) was much worse than has been reported [8] for the 4-nitro-isomer.

1-Nitro-2-styrylnaphthalene (55 mg.) in alcohol (10 ml.) was hydrogenated for 5 hr. at room temperature and pressure over palladium–charcoal. The solution was filtered and evaporated to yield crude 1-amino-2-phenethylnaphthalene (39 mg.) of lower m.p. (65—70°) than, but

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[3] A. H. Lamberton and P. T. McGrail, *J. Chem. Soc.*, 1963, 1776.
[4] P. P. T. Sah, *Rec. Trav. chim.*, 1940, **59**, 461.
[5] R. A. Abramovitch, D. H. Hey, and R. A. J. Long, *J. Chem. Soc.*, 1957, 1781.
[6] F. Mayer and T. Oppenheimer, *Ber.*, 1918, **51**, 1239.
[7] Varian High Resolution N.m.r. Catalog, National Press, 1962, spectra nos. 305 and 306.
[8] F. Bergmann and Z. Weinberg, *J. Org. Chem.*, 1941, **6**, 134.

otherwise identical with, material prepared by reduction with Raney nickel of 3-bromo-2-(1-nitro-2-napthyl)benzo-[*b*]thiophen. Acetylation of the crude amine (33 mg.) gave 1-acetamido-2-phenethylnaphthalene (22 mg.), m.p. 157—158°, identical with the material previously prepared.

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