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Electrophilic Substitution Reactions of Benzo[b]naphto[1,2-d]tiophene

Reakcje substytucji elektrofilowej benzo[b]nafto[1,2-d]tiofenu

Continuing the chemistry study of heterocyclic sulfur-containing compounds [1–4], this paper presents results of research on electrophilic substitution reactions of benzo[b]naphtho[1,2-d]thiophene.

Nitration of benzo[b]naphtho[1,2-d]thiophene with concentrated nitric acid in an acetic acid solution yielded 5-nitroderivative (1), which was oxidized by hydrogen peroxide into S,S-dioxyderivative (2). Reduction of compound (1) by stannous chloride in cyclohexanol yielded 5-aminocompound (3). The forming amine (3) was then transformed into acetyl (4) and benzoyl derivatives(5).

Benzo[b]naphtho[1,2-d]thiophene reacted with bromine in dry chloroform to afford 5-bromocompound (6), which was also prepared in the Sandmeyer reaction from amine (3). Bromide (6) was oxidized into sulfone (7) and also formed a Grignard reagent, which on treatment with dimethyl sulfate and carbon dioxide gave methylthioarene (8) and carboxylic acid (19) respectively. Acid (19) in the reaction with hydrogen peroxide formed sulfone acid (26). Acids (19) and (26) were characterized as they esters, amides and acid chlorides.

Acetylation of benzo[b]naphtho[1,2-d]thiophene with acetic anhydride and aluminium chloride in methylene chloride occurred without difficulties. Acetyl compound 9 was converted into E-oxime (10), and latter was transformed into

acetyl amine (4) by a Backmann rearrangement. By oxidation of the acetyl compound (9) with sodium hypobromite there was formed carboxylic acid (19).

In the further studies it was stated that benzo[b]naphtho[1,2-d]thiophene underwent a chloromethylation reaction with polyoxymethylene and hydrochloric acid in acetic acid to yield 5-chloromethyl compound (11). Condensation of 11 with thioglycolic acid afforded acid (13). Chloride (11) was converted by hexamethylenetetramine into 5-formyl derivative (12), which after oxydation with sodium hypobromite formed carboxylic acid (19).

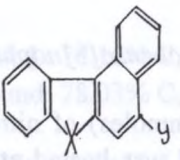
Benzo[b]naphtho[1,2-d]thiophene with chlorosulfonic acid afforded benzo[b]naphtho[1,2-d]thiophene-5-sulfonic acid (14), which was transformed into its chloride 15. Sulfonic acid chloride (15) heated with ammonia yielded amide (16). Chloride (15) was subjected to reaction to benzo[b]naphtho-[1,2-d]thiophene-5-sulfinic acid (17) in mild condition. Sulfinic acid (17) subjected to Peters reaction was transformed into 5-jodobenzo[b]naphtho-[1,2-d]thiophene (18). Jodo compound (18) via the Grignard derivative was converted into carboxylic acid (19), which was identical with acids obtained by bromination, nitration, acetylation and chloromethylation of tioarene.

Studying the ^{1}HNMR spectra for derivatives of benzo[b]naphtho-[1,2-d]thiophene (occurrence of singlet characteristic of position 5 or 6) it was stated that in electrophilic substitution reactions of benzo[b]naphtho[1,2-d]thiophene occurs in position 5 or 6.

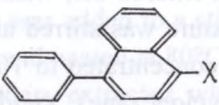
In order to exclude one of these positions desulfurization of benzo[b]-naphtho[1,2-d]thiophene-5-carboxylic acid to 1,4 phenyl naphthoic acid by means of Raney nickel was carried out. This way 1,4 phenyl naphthoic acid obtained from benzo[b]naphtho[1,2-d]thiophene-5-carboxylic acid univocally confirmed that electrophilic substitution reactions of benzo[b]naphtho[1,2-d]-thiophene occur in position 5.

EXPERIMENTAL

IR spectra were recorded in KBr discs with a FT 1725x Perkin Elmer spectrophotometer. ^{1}H-NMR spectra were determined using BF 567A Tesla 100 spectrometer with TMS as an internal standard.



1. x=S,	$y=NO_2$	17. x=S,	$y=SO_2H$
2. $x=SO_2$,	$y=NO_2$	18. x=S,	y=J
3. x=S,	$y=NH_2$	19. x=S,	y=COOH
4. x=S,	$y=NHCOCH_3$	20. x=S,	$y=COOCH_3$
5. x=S,	$y=NHCOC_6H_5$	21. x=S,	$y=COOC_2H_5$
6. x=S,	y=Br	22. x=S,	y=COCl
7. $x=SO_2$	y=Br	23. x=S,	$y=CONH_2$
8. x=S,	$y=CH_3$	24. x=S,	$y=CONHCH_3$
9. x=S,	$y=COCH_3$	25. x=S,	$y=CONHC_2H_5$
10. x=S,	$y=C(CH_3)=NOH$	26. $x=SO_2$,	y=COOH
11. x=S,	$y=CH_2Cl$	27. $x=SO_2$,	$y=COOCH_3$
12. x=S,	y=CHO	28. $x=SO_2$,	y=COCl
13. x=S,	$y=CH_2SCH_2COOH$	29. $x=SO_2$,	$y=CONH_2$
14. x=S,	$y=SO_3Na$	30. $x=SO_2$,	$y=CONHCH_3$
15. x=S,	$y=SO_2Cl$	31. $x=SO_2$,	$y=CONHC_2H_5$
16. x=S,	$y=SO_2NH_2$		



32. x=COOH	34. $x=COOC_2H_5$
33. $x=COOCH_3$	35. $x=CH_2OH$

Fig. 1. List of the newly obtained compounds

1. 5-Nitrobenzo[b]naphtho[1,2-d]thiophene (1)

Nitric acid (9.7 g, d=1.5) was added dropwise to a stirred solution of benzo[b]naphtho[1,2-d]thiophene (23.4 g, 0.1 mole) in glacial acetic acid (300 cm^3). After 1 h at room temperature the separated precipitate was filtered off and crystallized from CCl_4. Yellow needles, m.p. 174-175°C. Yield 22 g (78%).

Analysis:

For $C_{16}H_9NO_2S$ (279.32) calcd.: 68.80% C, 3.24% H, 5.01% N;
found: 68.62% C, 3.51% H, 5.04% N.

IR (cm^{-1}) 1336 ($\nu_s NO_2$), 1522 ($\nu_{as} NO_2$)

2. S,S-Dioxy-5-nitrobenzo[b]naphtho[1,2-d]thiophene (2)

The mixture of 1 g (3.5 mmoles) of nitrocompound 1 and 5 cm^3 of 30% H_2O_2 in 40 cm^3 of acetic acid was heated at 100°C for 1 h. The mixture was diluted with water (40 cm^3) and the separeted precipitate was filtered off. Yellow needles m.p. 258–259°C (from benzene). Yield 0.95 (87%).
Analysis:
For $C_{16}H_9NO_4S$ (311.32) calcd.: 61.73% C, 2.91% H, 4.50% N;
found: 61.58% C, 2.76% H, 4.38% N.
IR (cm^{-1}) 1341 ($\nu_s NO_2$), 1528 ($\nu_{as} NO_2$), 1130 ($\nu_s SO_2$), 1298 ($\nu_{as} SO_2$)

3. 5-Aminobenzo[b]naphtho[1,2-d]thiophene (3)

A sample of 13.97 g (50 mmoles) of nitro 1, 36.1 (0.16 mole) of $SnCl_2 \cdot 2H_2O$, 70 cm^3 of HCl and 300 cm^3 of cyclohexanol was refluxed for 1 h. After cooling the precipitate was filtered off, washed with water and added to 300 cm^3 of 30% NaOH. The mixture was stirred at 40°C for 1 h and extracted with benzene. The solution was concentrated to 70 cm^3 and amine filtered off. Needles m.p. 134–135°C (from cyclohexane). Yield 11 g (88%).
Analysis:
For $C_{16}H_{11}NS$ (249.34) calcd.: 77.08% C, 4.45% H, 5.62% N;
found: 77.32% C, 4.52% H, 5.51% N.

4. 5-Acetylaminobenzo[b]naphtho[1,2-d]thiophene (4)

A sample of 3.75 g (15 mmoles) of amine 3, 1.53 g of acetic anhydride in 50 cm^3 of benzene was refluxed for 1 h. The precipitate was filtered off and crystallized from ethanol. Needles, m.p. 278–279°C. Yield 3.5 g (80%).
Analysis:
For $C_{18}H_{13}NOS$ (291.37) calcd.: 74.20% C, 4.50% H, 4.81% N;
found: 73.95% C, 4.26% H, 4.96% N.

5. 5-Benzoylaminobenzo[b]naphtho[1,2-d]thiophene (5)

Amine 3 (0.62 g, 2.5 mmoles) with benzoyl chloride (0.35 g, 2.5 mmoles) was converted into benzoyl amine 5. Needles, m.p. 263–264°C (from ethanol). Yield 0.63 g (74%).

Analysis:
For $C_{23}H_{15}NOS$ (353.45) calcd.: 78.16% C, 4.28% H, 3.96% N;
found: 78.03% C, 4.07% H, 4.13% N.

6. 5-Bromobenzo[b]naphtho[1,2-d]thiophene (6)

Method a

Bromine (8 g, 0.1 mole) was added dropwise to a vigorously stirred solution of benzo[b]naphtho[1,2-d]thiophene (11.7 g, 50 mmoles) in dry chloroform (80 cm^3). The mixture was stirred at room temperature for 1 h. The separated precipitate was filtered off, washed with water and crystallized from benzene–hexane (1:1). Needles, m.p. 162–163°C. Yield 11.2 g (72%).

Method b

The sample of 5 g (20 mmoles) of amine 3 was transformed into diazocompound. The diazocompound was added to a stirred solution of cuprous bromide (6 g) in 50 cm^3 of 40% HBr and heated at 80°C for 1 h. The solution was diluted with water (400 cm^3) and then, extracted with benzene. The solvent was removed and the residue was crystallized. Yield 3 g (48%).
Analysis:
For $C_{16}H_9BrS$ (313.22) calcd.: 61.36% C, 2.90% H;
found: 61.35% C, 2.80% H.

7. S,S-dioxy-5-bromobenzo[b]naphtho[1,2-d]thiophene (7)

A sample of 0.94 g (3 mmoles) of bromine 6 was oxidized into sulfone as in section 2. Pale yellow needles, m.p. 312–313°C (from benzene). Yield 0.85 g (82%).
Analysis:
For $C_{16}H_9BrO_2S$ (345.22) calcd.: 55.67% C, 2.63% H;
found: 55.73% C, 2.58% H.
IR (cm^{-1}) 1138 ($\nu_s SO_2$), 1286 ($\nu_{as} SO_2$).

8. 5-Methylbenzo[b]naphtho[1,2-d]thiophene (8)

A mixture of 6.26 g (20 mmoles) of bromine 6 or iodide and 1.42 g (10 mmoles) of methyl iodide in 80 cm^3 of benzene was added dropwise to

0.97 g of magnesium im 50 cm^{3} of diethyl ether and refluxed for 2.5 h. Then dimethyl sulfate (12.6 g, 0.1 mole) was added and refluxed for 1 h. After dilution in 3% HCl (200 cm^3) the mixture was extracted with benzene. Benzene was removed and 50 cm^3 of ethanol, 50 cm^3 of 20% aqueous NaOH solution were added to the residue and refluxed for 25 min. The solution was diluted with 500 cm^3 of water, then the precipitate was filtered off and crystallized from cyclohexane. Plates, m.p. 127.5–128.5°C ((ref. [5] t_t 127–128°C). Yield 3.7 g (74%).

Analysis:

For $C_{17}H_{12}S$ (244.35) calcd.: 82.22% C, 4.87% H, 12.91% S;
found: 82.09% C, 4.59% H, 12.73% S.

IR (cm^{-1}) 2875 ($\nu_s CH_3$), 2958 ($\nu_{as} CH_3$).

^{1}HNMR ppm ($CDCl_3$); 2.67 S 3H(CH_3), 7.32–7.72 m 5H(2,3,6,9,10), 7.75–8.1 m 2H(4,8), 8.6–8.97 m 2H(1,11).

9. 5-Acetylbenzo[b]naphtho[1,2-d]thiophene (9)

A mixture of acetic anhydride (5.1 g, 50 mmoles 1) $AlCl_3$ (17 g) and methylene chloride (20 cm^3) was added to the solution of benzo[b]naphtho[1,2-d]-thiophene (11.71 g, 50 mmoles) in 100 cm^3 of methylene chloride. The mixture was poured on ice and extracted with methylene chloride. The solvent was removed and the residue was separated on Al_2O_3 column with benzene. Needles, m.p. 147–148°C (from ethanol). Yield 8.3 g (60%).

Analysis:

$C_{18}H_{12}OS$ (276.35) calcd.: 78.23% C, 4.38% H, 11.60% S;
found: 78.01% C, 4.49% H, 11.29% S.

IR (cm^{-1}) 16885(ν C=O), 2865 ($\nu_s CH_3$), 2939 ($\nu_{as} CH_3$).

^{1}HNMR ($CDCl_3$); 2.78 S 3H(CH_3), 7.47–7.7 m 4H(2,3,9,10), 7.25–8.00 m 2H(4,8), 8.23 S 1H(6), 8.77–9.00 m 2H(1,11) – D.

2,4-dinitrophenylhydrazone. Orange needles m.p. 293–294°C (from benzene).

10. E Oxime of 5-acetylbenzo[b]naphtho[1,2-d]thiophene (10)

The mixture of 2.76 g (10 mmoles) of compound 9, 1.39 g (20 mmoles) of hydroxylamine hydrochloride and 3.5 cm^3 of dry pyridine in 30 cm^3 of ethanol was refluxed for 2 h. The precipitate was filtered off, washed with water and crystallized from ethanol. Plates, m.p. 208.5–210 cm^3. Yield 2.63 g (90%).

Analysis:
For $C_{18}H_{13}NOS$ (291.37) calcd.: 74.20% C, 4.50% H, 4.81% N;
found: 74.06% C, 4.65% H, 4.82% N.

11. Beckmann rearrangement of E oxime 10

The sample of 2.91 g (10 mmoles) of oxime 10 and 3 cm^3 of $SOCl_2$ in 50 cm^3 of ether was refluxed until the precipitate was dissolved completely. After removing the solvents under the reduced pressure to the residue 50 cm^3 of water was added. The mixture was boiled for 5 min and then acetylamine 4 was filtered off. Needles, m.p. 278–279°C. Yield 2.7 g (94%).

12. 5-Chloromethylbenzo[b]naphtho[1,2-d]thiophene (11)

A mixture of 5.8 g (25 mmoles) of benzo[b]naphtho[1,2-d]thiophene, 2 g of polyoxymethylene, 20 cm^3 of conc. HCl, 10 cm^3 H_3PO_4 (d=1.7) and 80 cm^3 of acetic acid was heated at 65°C for 15 h. The precipitate was filtered off and crystallized from cyclohexane. Needles, m.p. 225–228°C. Yield 4.2 g (60%).
Analysis:
For $C_{17}H_{11}ClS$ (282.79) calcd.: 72.20% C, 3.92% H, 12.54% Cl;
found: 72.45% C, 4.20% H, 12.28% Cl.

13. 5-Formylbenzo[b]naphtho[1,2-d]thiophene (12)

The solution of 3.34 g (24 mmoles) of hexamethylenetetramine in 30 cm^3 of chloroform was added to the boiling of 5.62 g (20 mmoles) of 11 in 100 cm^3 of chloroform and refluxed for 1 h. After cooling the salt was filtered off (m.p. 187–188°C decomp.). The mixture of salt and 60 cm^3 of 50% acetic acid was refluxed for 2 h and then 10 cm^3 of conc. HCl was added to it. It was refluxed for 10 min. again. Pale yellow needles m.p. 71–72°C (cyclohexane). Yield 3.7 g (69%).
Analysis:
For $C_{17}H_{10}OS$ (262.33) calcd.: 77.84% C, 3.84% H, 12.22% S;
found: 77.98% C, 3.73% H, 12.61% S.
IR (cm^{-1}) 1696 (ν C=OCHO).
^{1}HNMR 7.35–7.73 m 4H(2,3,9,10), 7.85–7.99 m 2H(4,8), 8.47 S 1H(6),
8.59–8.85 m 2H(1,11), 10.28 S 1H(CHO).
2,4-Dinitrophenylhydrazone orange needles m.p. 210–212°C (ethanol).

14. Benzo[b]naphtho[1,2-d]thiophene-5-methylthioglycolic acid (13)

The neutralized solution of 1.84 g (20 mmoles) of tioglicolic acid with NaOH in 20 cm^3 water was added to 5.65 g (20 mmoles) of 11 in 150 cm^3 of ethanol. The mixture was refluxed for 1 h. After removing the ethanol, the residue was washed (2*100 cm^3) with boiling water. The aqueous layer was acidified with conc. HCl. Needles m.p. 112–114°C (cyclohexane). Yield 4.4 g (67%).
Analysis:
For $C_{19}H_{14}O_2S_2$ (338.45) calcd.: 67.43% C, 4.17% H, 18.95% S;
found: 67.21% C, 3.98% H, 19.26% S.

15. Sodium benzo[b]naphtho[1,2-d]thiophene-5-sulfonate (14)

Chlorosulfonic acid (4.7 g 40 mmoles) was added dropwise to a vigorously stirred solution of 9.7 g (40 mmoles) of benzo[b]naphtho[1,2-d]thiophene in 120 cm^3 of dry chloroform at -5°C. The mixture was kept at this temperature for 30 min. and was added 6 g NaOH in 100 cm^3 water. The precipitate was filtered off and crystallized from water. Plates. Yield 9.1 g (81%).

16. Benzo[b]naphtho[1,2-d]thiophene-5-sulfochloride (15)

The mixture of 14 (15 g) and 18 g of PCl_5 was heated at 100°C for 1 h. The reaction mixture was poured into ice and precipitate filtered off. Needles, m.p. 214–215°C (cyclohexane-benzene 1:2). Yield 12 g (80%).
Analysis:
For $C_{16}H_9ClO_2S_2$ (332.85) calcd.: 57.74% C, 2.73% H, 10.65% Cl;
found: 57.46% C, 2.90% H, 11.12% Cl.
IR (cm^{-1}) 1168 ($\nu_s SO_2$).

17. Benzo[b]naphtho[1,2-d]thiophene-5-sulfamide (16)

Needles, m.p. 155–156°C (cyclohexane).
Analysis:
$C_{16}H_{11}NO_2S$ (313.40) calcd.: 61.32% C, 3.54% H, 4.47% N;
found: 61.43% C, 3.32% H, 4.29% N.

18. Benzo[b]naphtho[1,2-d]thiophene-5-sulfinic acid (17)

The sample of 16.64 g (50 mmoles) of powdered sulfochloride 15 was added in small portion to a boiling solution of 7.56 g (60 mmoles) of Na_2SO_3 and 7.42 g (70 mmoles) of Na_2CO_3 in 250 cm^3 water. The mixture was boiled for 30 min. After cooling the solution was acidified with conc. HCl and acid was filtered off. Needles, m.p. 192–195°C (acetic acid). Yield 12 g (80%).
Analysis:
For $C_{16}H_{10}O_2S_2$ (298.37) calcd.: 64.41% C, 3.38% H, 21.50% S;
found: 64.63% C, 3.21% H, 21.79% S.
IR (cm^{-1}) 1098 (ν S=O).

19. 5-Iodobenzo[b]naphtho[1,2-d]thiophene (18)

The solution of 8 g (25 mmoles) of sodium salt of 17 in 500 cm^3 of boiling water was added to a vigorously stirred solution of 8.15 g (30 mmoles) of $HgCl_2$ and 0.1 g of $NaHCO_3$ in 250 cm^3 of water. The suspension was heated until the evolution of SO_2 ceased (ca 2 h). After cooling the precipitate was filtered off and after washing with water and ethanol, it was added to 110 cm^3 of ethanol. The suspension was heated, and the solution of 9.8 g KI and 14.1 g I_2 in 14 cm^3 of water was slowly added dropwise to it, and stirring until the mercury compound was almost completely dissolved and the liquid become pale yellow. Ethanol was removed and the precipitate was filtered off and washed solution KI. Lumps, m.p. 114–116°C (acetone). Yield 5 g (27%).
Analysis:
For $C_{16}H_9IS$ (360.21) calcd.: 53.35% C, 2.52% H;
found: 53.52% C, 2.70% H.

20. Benzo[b]naphtho[1,2-d]thiophene-5-carboxylic acid (19)

Method a

The sample of 31.32 g (0.1 mole) of bromine 6 or 36.02 g (0.1 mole) of Iodide 18 was converted into magnesium compound as in section 8. After cooling to -20°C it was saturated with vigorous stream of dry CO_2 (2 h) and then the solution of 300 cm^3 of 5% HCl was added. Organic solvents were removed. The precipitate was filtered off. Then it was dissolved in 200 cm^3 of 5% NaOH so-

lution. Sodium salt was separated, dissolved in 200 cm^3 water and acidified with conc. HCl. Needles, m.p. 319–320°C (dioxane). Yield 24 g (88%).

Method b

The solution of 2.76 g (10 mmoles) of acetyl compound 9 or 2.62 g (10 mmoles) of aldehyde 12 was dissolved in 200 cm^3 dioxane. NaBrO solution (prepared from 8 g bromine and 4.5 g of NaOH in 50 cm^3 of water) was added to it and the mixture was stirred at room temperature for 16 h. The solution was diluted with 300 cm^3 of water and extracted with benzene. The aqueous solution was acidified with HCl. Yield 1.7 g (64%).

Analysis:

For $C_{17}H_{10}O_2S$ (278.33) calcd.: 73.36% C, 3.62% H, 11.52% S;
found: 73.61% C, 3.55% H, 11.17% S.

IR (cm^{-1}) 17.02 ν C=O (COOH).

21. Methyl ester of benzo[b]naphtho[1,2-d]thiophene-5-carboxylic acid (20)

The mixture of acid 19 in benzene with etheral solution of diazomethane was converted into its methyl ester. Needles m.p. 136–137°C (cyclohexane). Yield 95%.

Analysis:

For $C_{18}H_{12}O_2S$ (292.36) calcd.: 73.95% C, 4.14% H;
found: 73.89% C, 3.98% H.

^{1}HNMR 4.00 s 3H(CH_3), 7.35–7.73 m 4H(2,3,9,10), 7.84–7.99 m 2H(4,8), 8.47 S 1H(6), 8.59–8.84 m 2H(1,11).

22. Ethyl ester of benzo[b]naphtho[1,2-d]thiophene-5-carboxylic acid (21)

Acid 19 was converted into its ethyl ester as in section 20. Prism m.p. 105–106°C (hexane). Yield 94%.

Analysis:

For $C_{19}H_{14}O_2S$ (306.39) calcd.: 74.48% C, 4.61% H;
found: 74.41% C, 4.92% H.

23. Chloride of benzo[b]naphtho[1,2-d]thiophene-5-carboxylic acid (22)

The mixture of 2.78 g (10 mmoles) of acid 19 and 20 cm^3 of $SOCl_2$ was heated until the precipitate almost completely dissolved (1 h). Thionyl chloride

was removed and the residue was crystallized from dry benzene. Yellow needles m.p. 168–170°C. Yield 2.6 g (89%).
Analysis:
For $C_{17}H_9ClOS$ (296.78) calcd.: 68.80% C, 3.06% H, 11.95% S;
found: 68.61% C, 3.29% H, 11.93% S.

24. Preparation of N-substituted amides

The mixture 2.97 g (10 mmoles) of chloride 22 and 20 cm^3 of 20% aqueous solution of amine was stirred at room temperature for 30 min. The precipitate was filtered and washed with water.

25. Amide of benzo[b]naphtho[1,2-d]thiophene-5-carboxylic acid (23)

Needles, m.p. 297.5–288°C (methanol). Yield 80%.
Analysis:
For $C_{17}H_{11}NOS$ (277.35) calcd.: 73.62% C, 5.00% H, 5.05% N;
found: 73.80% C, 3.85% H, 4.96% N.

26. N Methylamide of benzo[b]naphtho [1,2-d]thiophene-5-carboxylic acid (24)

Needles, m.p. 245–245.5°C (benzene). Yield 92%.
Analysis:
For $C_{18}H_{13}NOS$ (291.37) calcd.: 74.20% C, 4.50% H, 4.81% N;
found: 74.35% C, 4.39% H, 4.75% N.

27. N Ethylamide of benzo [b]naphtho[1,2-d]thiophene-5-carboxylic acid (25)

Needles, m.p. 220–221.5°C (benzene). Yield 89%.
Analysis:
For $C_{19}H_{15}NOS$ (305.40) calcd.: 74.72% C, 4.95% H, 4.59% N;
found: 74.58% C, 4.84% H, 4.81% N.

28. S,S-dioxybenzo[b]naphtho[1,2-d]thiophene-5-carboxylic acid (26)

Acid 19 (2.78 g, 10 mmoles) was oxidized to sulfon as in section 2. Pale yellow prisms, m.p. 328–330°C (acetic acid). Yield 2.7 g (87%).
Analysis:

For $C_{17}H_{10}O_4S$ (310.33) calcd.: 65.80% C, 3.25% H, 10.33% S;
found: 65.77% C, 3.07% H, 10.01% S.
IR (cm^{-1}) 1715 (ν C=OCOOH), 1156 ($\nu_s SO_2$), 1304 ($\nu_s SO_2$).

29. Methyl ester of S,S-dioxybenzo[b]naphtho[1,2-d]thiophene-5-carboxylic acid (27)

Plates m.p. 206–207°C (ethanol). Yield 88%.
Analysis:
For $C_{18}H_{12}O_4S$ (324.36) calcd.: 66.65% C, 3.73% H, 9.88% S;
found: 66.60% C, 3.99% H, 10.07% S.
IR (cm^{-1}) 1712 (C=O), 1152 ($\nu_s SO_2$), 1305 ($\nu_s SO_2$).

30. Chloride of S,S-dioxybenzo[b]naphtho[1,2-d]thiophene-5-carboxylic acid (28)

Yellow prisms, m.p. 252–253°C (benzene). Yield 84%.
Analysis:
For $C_{17}H_9ClO_3S$ (328.78) calcd.: 62.17% C, 2.76% H, 10.77% Cl;
found: 62.36% C, 2.61% H, 10.41% Cl.

31. Amide of S,S-dioxybenzo[b]naphtho[1,2-d]thiophene-5-carboxylic acid (29)

Yellow prisms, m.p. 333–335°C (decomp.) (methanol). Yield 82%.
Analysis:
For $C_{17}H_{11}NO_3S$ (309.35) calcd.: 66.01% C, 3.58% H, 4.53% N;
found: 66.25% C, 3.39% H, 4.62% N.

32. N-methylamide of S,S-dioxybenzo[b]naphtho[1,2-d]thiophene-5-carboxylic acid (30)

Yellow prisms, m.p. 283–284°C (methanol). Yield 92%.
Analysis:
For $C_{18}H_{13}NO_3S$ (323.37) calcd.: 66.86% C, 4.05% H, 4.33% N;
found: 66.99% C, 3.85% H, 4.34% N.

33. N-ethylamide of S,S-dioxybenzo[b]naphtho[1,2-d]thiophene-5-carboxylic acid (31)

Yellow prisms, m.p. 269–270°C (methanol).

Analysis:

For $C_{19}H_{15}NO_3S$ (327.40) calcd.: 67.64% C, 4.48% H, 4.15% N;
found: 67.86% C, 4.53% H, 4.13% N.

34. Desulfurization of benzo[b]naphtho[1,2-d]thiophene-5-carboxylic acid (32)

The mixture of 2.78 g (10 mmoles) of acid 19, 2.1 g (20 mmoles) of Na_2CO_3 and 8.38 g of the Raney nickel in 300 cm^3 of water was heated to 75°C for 50 min. The precipitate was filtered off and washed with hot solution of 5% Na_2CO_3. The solution was acidified with conc. HCl and 1,4-phenylnaphthoic acid (32) was filtered off and crystallized from 50% acetic acid. Prisms, m.p. 171.5–172.5°C (ref. 6 t_l 172–173°C). Yield 1.6 g (65%).

Analysis:

For $C_{17}H_{12}O_2$ (248.28) calcd.: 82.24% C, 4.86% H;
found: 82.22% C, 4.99% H.

^{1}HNMR 7.45–7.68 m 3H(3,6,7), 7.5 s 5H(C_6H_5), 7.96 dd, J=8.7 Hz 1H(5), 8.46 d, J=7.6 Hz 1H(2), 8.20 dd, J=8.5 Hz 1H(8), 11.59 s 1H(COOH).

35. Methyl ester of 1,4 phenylnaphthoic acid (33)

Prisms, m.p. 80.5–81.5°C (hexane). Yield 92%.

Analysis:

For $C_{18}H_{14}O_2$ (262.31) calcd.: 82.42% C, 5.38% H;
found: 82.77% C, 5.18% H.

36. Ethyl ester of 1,4 phenylnaphthoic acid (34)

Prisms m.p. 34–35°C (hexane). Yield 90%.

Analysis:

For $C_{19}H_{16}O_2$ (276.23) calcd.: 82.59% C, 5.84% H;
found: 82.40% C, 6.04% H.

37. 1,4 phenylnaphthylmathanol (35)

The solution of 2.48 g (10 mmoles) of acid 32 in 200 cm^3 ether was added to the mixture of 0.8 g $LiAlH_4$ in 50 cm^3 ether. The mixture was refluxed for 30 min, poured into 200 cm^3 5% HCl and extracted with ether. Solvent was removed and the residue was crystallized from hexane. Prisms m.p. 81–81.5°C. Yield 1.8 g (65%).

Analysis:

For $C_{17}H_{14}O$ (234.29) calcd.: 87.15% C, 6.02% H;
found: 87.32% C, 6.20% H.

^{1}HNMR, 2.64 s 1H(OH), 5.02 s 2H(CH_2), 7.32–7.50 m 4H(2,3,6,7), 7.39 s 5H (C_6H_5), 7.84–8.11 m 2H(5,8).

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STRESZCZENIE

Badano reakcje substytucji elektrofilowej benzo[b]nafto[1,2-d]tiofenu, takie jak: nitrowanie, bromowanie, acetylowanie, chlorometylowanie i sulfonowanie.

Udowodniono, iż w reakcjach substytucji elektrofilowej podstawnik zajmuje położenie 5.