Pyridine *N*-Sulfides. Benzisothiazolo[2,3-*a*]pyridinium Tetrafluoroborates and Benzothiopheno[3,2-*b*]pyridines. Novel Heterocyclic Systems

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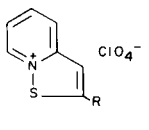
2-(2-Mercaptophenyl)pyridines are prepared from the corresponding phenols and oxidized with *N*-chlorosuccinimide and silver tetrafluoroborate to benzisothiazolo[2,3-*a*]pyridine salts (**4**). The latter do not rearrange thermally or photochemically to benzothiopheno[3,2-*b*]pyridines (**19**) and are attacked by nucleophiles at sulfur rather than in the pyridine ring, to give the original 2-(2-mercaptophenyl)pyridine back in a reaction involving a dismutation. **19** is prepared by rearranging *O*-[2-(3-bromo-2-pyridyl)-4-nitrophenyl]dimethylthiocarbamate to the *S*-aryl compound and heating the latter with strong base.

J. Heterocyclic Chem., **19**, 509 (1982).

In contrast to the chemistry of six-membered heteroaromatic *N*-oxides, that of the corresponding *N*-sulfides is uncharted as far as we can tell. Indeed, very little is known about *N*-thiopyridinium salts of any description, whereas *N*-alkoxy- and -aryloxypyridinium salts are well documented (1). The same applies to fused ring systems containing the *N*-thiopyridinium linkage. Of the very few known, the best studied are the isothiazolo[2,3-*a*]pyridinium perchlorates (**1**), obtained (2) by the oxidation of 2-pyridylmethylthioketones, and the 2-amino[1,2,4]thiadiazolo[2,3-*a*]pyridinium salts (**2**), obtained by the oxidation



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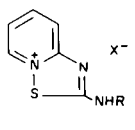

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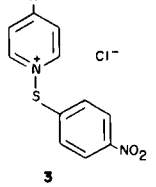

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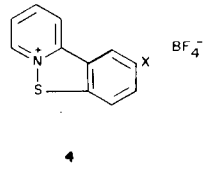
of *N*-(2-pyridyl)thioureas (3). The first authenticated simple *N*-arylthiopyridinium salts (**3**) have now been reported and some of their chemistry described (4). The structure of the product $S_2Cl_2.2C_5H_5N$ from pyridine and sulfur monochloride was shown to be *N,N'*-dithiodipyridinium dichloride $(C_5H_5N^+\text{-}S\text{-})_2\ 2Cl^-$ (4).

We now report the synthesis and characterization of the novel tricyclic system (**4**) which is essentially the "intramolecular" version of an *N*-arylthiopyridinium salt (**3**). *N*-Aryloxypyridinium tetrafluoroborates (**5**) undergo base-catalyzed rearrangement to 2-*o*-hydroxyarylpyridines (**6**) (5). 2-(2-Hydroxy-5-nitrophenyl)pyridine (**6**, R = H, X = NO_2) was converted into the corresponding thiol (**7**; R = H, X = NO_2) by a modification of Newman's procedure (6). We found that yields improved appreciably (to 55% for **7**, and 64% for **11**) if the intermediate *S*-arylthiocarbamates (**9**) (formed by heating **8**) were isolated and hydrolyzed with 2*N* hyrochloric acid instead of using base.



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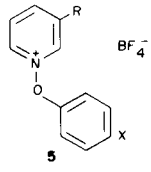

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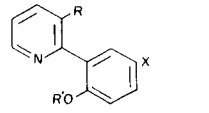
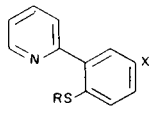




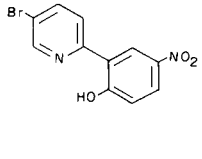
6, R' = H
8, R' = $CNMe_2$ (=S)
23, R = R' = H, X = NO_2

7, R = H, X = NO_2
9, R = $CNMe_2$ (=O), X = NO_2
10, R = $CNMe_2$ (=O), X = CN
11, R = H, X = CN
12, R = Cl, X = NO_2
13, R = Cl, X = CN
14, R = H, X = NH_2

Treatment of **7** with *N*-chlorosuccimide (NCS) in benzene solution under dry nitrogen at 0-5° converted it to the sulfenyl chloride (12) which could only be isolated in very crude form. Contaminating succinimide could not be completely removed. The crude sulfenyl chloride was therefore converted directly *in situ* to 7-nitrobenzisothiazolo[2,3-*a*]pyridinium tetrafluoroborate (**4**, X = NO_2) (60%) by the addition of an equivalent of silver tetrafluoroborate in acetonitrile. Hot methanol effected the separation of **4** from silver chloride in succinimide. Similarly, 2-(4-cyano-2-mercaptophenyl)pyridine (**11**) was converted to the sulfenyl chloride (**13**) and thence to 7-cyanobenzisothiazolo[2,3-*a*]pyridinium tetrafluoroborate (**4**, X = CN) (56.5%).

3-Bromo-1-(4-nitrophenoxy)pyridinium tetrafluoroborate (**5**, R = Br, X = NO_2) was prepared (59.3%) as usual from the *N*-oxide and *p*-nitrobenzenediazonium tetra-

fluoroborate. Base-catalyzed rearrangement with potassium phenoxide in acetonitrile gave a mixture of **6** (R = Br) (60%) and **15** (< 1%). The orientation of the products were confirmed by nmr spectroscopy: for **6** (R = Br) δ 8.52 (dd, 1H, $J_{5,6}$ = 5.5 Hz, $J_{4,6}$ = 1.6 Hz) corresponding to H_6 and indicating the 2,3-disubstitution pattern in the pyridine ring; for **15**, δ 9.0 (d, 1H, $J_{4,6}$ = 2 Hz), also corresponding to H_6, and establishing the 2,5-disubstitution of the pyridine ring in **15**. Separation of **6** and **15** was easily achieved on a column of silcia gel. The predominant formation of the rearrangement product in which the migrating group enters the vacant position ortho to the 3-bromo substituent was expected on the basis of the kinetics of base-catalyzed H-D exchange in 3-bromopyridine 1-oxide with 0.1*N* sodium deuteroxide in deuterium oxide (7). At 5° only C-2-H exchanged readily, whereas at 50°, exchange at C-2 was too rapid to measure, but exchanges at C-6 and C-4 could be followed. The *pseudo*-first order rate constants were: $k(5°)_{H\text{-}2} = 1.7 \times 10^{-4}$ sec^{-1}; $k(50°)_{H\text{-}6} = 3.9 \times 10^{-5}$ sec^{-1}; $k(50°)_{H\text{-}4} = 4.6 \times 10^{-6}$ sec^{-1}; no exchange at C-5 was observed. Consequently, treatment of **5** (R = Br) with base should lead to the preferential formation of carbanion **16** over that of **17** and hence to more **6** (R = Br) then **15**.



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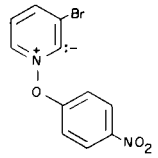

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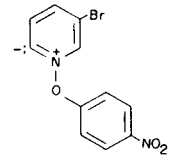

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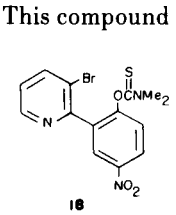
Phenol **6** (R = Br) gave the desired *O*-[2-(3-bromo-2-pyridyl)-4-nitrophenyl]dimethylthiocarbamate (**18**) (52%) on treatment with dimethylthiocarbamoyl chloride and sodium hydroxide. When the latter was heated at 190-195° to rearrange it to the *S*-phenyldimethylthiocarbamate and the resulting mixture heated with potassium hydroxide in aqueous ethylene glycol the product isolated in near quantitative yield was 7-nitrobenzothiopheno[3,2-*b*]pyridine (**19**). This compound was needed as an authentic sample of a possible product that would be formed *via* an arylsulfenium ion in the thermolysis of **4**.



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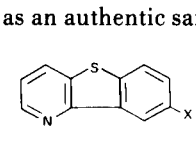
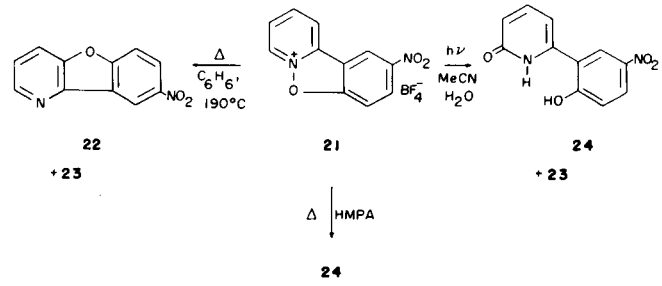


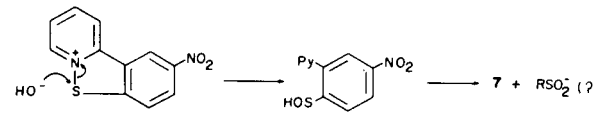
19, X = NO_2
20, X = NH_2

Reduction of **19** with stannous chloride-hydrogen chloride gave the primary amine **20**. Initially, the mass spectrum of this compound suggested that over-reduction had occurred and that the product might be 2-(5-amino-2-mercaptophenyl)pyridine (**14**). Thus, the mass spectrum gave a base peak of m/e 200 corresponding to M^+, but the (M + 1) peak at m/e 201 had a relative intensity of 91%, m/e 202 (34%) (M + 2), 203 (3.9%), 204 (6.7%). The nmr spectrum is consistent with structure **20**, however, showing only one pyridine β-proton and two exchangeable protons (NH_2). Elemental analysis was consistent with the proposed structure. We could not find any precedent for such unusually intense (M + 1) and (M + 2) peaks in sulfur compounds which peaks, presumably, arise by facile ion-molecule reactions in the amine (8).

The arylthiopyridinium salt **4** (X = NO_2) behaves quite differently from its oxygen counterpart **21**. Thus, **21** undergoes thermal rearrangement to 7-nitrobenzofuro-[3,2-*b*]pyridine (**22**), while thermolysis in HMPA or photolysis in aqueous acetonitrile gave 6-(2-hydroxy-5-nitrophenyl)-2-pyridone (**24**) (9). On the other hand, heating **4** (X = NO_2) at 190° in benzene, benzonitrile, or nitromethane either gave back **4** or an intractable brown residue in which no **19** could be detected. Again, in contrast to the oxygen compound, **4** (X = NO_2) was unchanged on irradiation (3000 Å) in acetonitrile. Treatment of **4** (X = NO_2) with *cold* aqueous sodium hydroxide solution of with HMPA at 120-125° or with a boiling solution of sodium azide in acetonitrile gave, in each case, the original thiophenol **7** (64, 50, and 78% yield, respectively). No other pure product could be isolated from these reactions.



A possible route to **7** from the reaction of **4** with base is the nucleophilic atack by OH^- at sulfur concomitant with $^+$N-S bond cleavage leading to the sulfenic acid **25** which dismutates (10) to the corresponding thiol (**7**) and sulfenic acid. Attempts were made to isolate and purify the latter and, though a sodium salt was isolated, it could not be purified sufficiently for analysis and characterized. Similar mechanisms may be written for attack by N_3^- or HMPA at sulfur (11). Since more than 50% of **7** is isolated



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in some cases this is not an ordinary disproportionation. Nucleophilic attack thus takes place at the sulfur atom — and not in the pyridine ring as it does with aryloxypyridinium salts (9). This is similar to what has been observed with **1** (2) and **2** (3), as well as with *N,N'*-dithiodipyridinium dichloride and with **3** (4). If a sulfenium ion (9) is produced by the thermolysis of **4** (X = NO_2) (*cf.* thermolysis of **21** in which an aryloxenium ion is generated (9)) then it must not be electrophilic enough to attack the pyridine ring at carbon and give **19**.

EXPERIMENTAL

O-[2-(2-Pyridyl)-4-nitrophenyl]dimethylthiocarbamate (**8**, R = H, X = NO_2).

A solution of dimethylthiocarbamoyl chloride (0.50 g) in dry tetrahydrofuran (5 ml) was added dropwise over a period of 15 minutes to a solution of 2-(2-hydroxy-5-nitrophenyl)pyridine (0.65 g) and potassium hydroxide (0.28 g) in water (10 ml) at 5°. The solution was then stirred at room temperature for 45 minutes, 10% aqueous potassium hydroxide (10 ml) added, and the mixture extracted with benzene (4 × 20 ml). The extracts were combined, washed with saturated aqueous sodium chloride solution, dried (magnesium sulfate) and evaporated to give the product which was recrystallized from ether and gave yellow crystals (0.55 g, 60%), mp 107-108°; ir (potassium bromide): 1560-1490, 1345 cm^{-1}; nmr (carbon disulfide): δ 8.7-8.45 (m, 2H, H_6 and H_A), 8.1 (dd, 1H, J_{AB} = 2.5 Hz, J_{BC} = 9 Hz, H_B), 7.7-7.45 (m, 2H, H_4 and H_C), 7.3-7.0 (m, 2H, H_5 and H_3), 3.22 (s, 3H, CH_3).

Anal. Calcd. for $C_{14}H_{13}N_3O_3S$: C, 55.45; H, 4.29. Found: C, 55.39, H, 4,34.

The following were prepared in a similar manner.

O-[4-Cyano-2-(2-pyridyl)phenyl]dimethylthiocarbamate (**8**, R = H, X = CN).

This compound was obtained in a yield of 60.7%, mp 113-113.5° (from ethanol); ir (potassium bromide): 2230 cm^{-1} (C≡N).

Anal. Calcd. for $C_{15}H_{13}N_3OS$: C, 63.57; H, 4.63. Found: C, 63.58; H, 4.63.

O-[2-Cyano-6-(2-pyridyl)phenyl]dimethylthiocarbamate.

This compound was obtained in a yield of 75.9%, mp 129-130° (from ethanol); ir (potassium bromide): 2230 cm^{-1} (C≡N); nmr (deuteriochloroform): δ 8.7 (d, 1H, $J_{3,4}$ = 5 Hz, H_4), 7.94 (dd, 1H, J_{AB} = 7.5 Hz, J_{AC} = 2 Hz, H_A), 7.8-7.1 (m, 5H, H_B, H_C, H_1, H_2, H_3), 3.32 (s, 6H, $2CH_3$); ms: m/e 283 ($M^{\cdot}$), 239 ($M^{\cdot}$-NMe_2), 211 ($M^{\cdot}$-$CONMe_2$).

Anal. Calcd. for $C_{15}H_{13}N_3OS$: C, 63.60; H, 4.59. Found: C, 63.54; H, 4.64.

O-[2-(2-Pyridyl)-6-trifluoromethylphenyl]dimethylthiocarbamate.

This compound was obtained in a yield of 36%, mp 83.5-84°.

Anal. Calcd. for $C_{15}H_{13}F_3N_2OS$: C, 55.21; H, 3.99. Found: C, 55.24; H, 4.04.

S-[2-(2-Pyridyl)-4-nitrophenyl]dimethylthiocarbamate (**9**).

The *O*-arylthiocarbamate (**8**, R = H, X = NO_2) (0.43 g) was heated under nitrogen at 190-200° for 1 hour. The product was dissolved in acetone (15 ml), decolorized with charcoal, filtered through Celite and the filtrate concentrated down to 10 ml. Light petroleum was added to the cloud point to give an oil which crystallized and was washed with cold ether to give **9** (249 mg, 58%), mp 111-114°, depressed on admixture with **8**; ir (Nujol): 1655 (C=O), 1505, 1335 cm^{-1} (NO_2). It was not purified further but used directly in the hydrolysis step.

2-(2-Mercapto-5-nitrophenyl)pyridine (**7**).

(a) By Acid Hydrolysis of **9**.

The *S*-arylthiocarbamate (**9**) (1.76 g) was dissolved in 2*N* hydrochloric acid (35 ml) and the solution heated under reflux for 3.5 hours. It was cooled and brought to *p*H ~ 4 with 4*N* sodium hydroxide. The yellow thiol (585 mg), mp 166-170°, separated and was filtered. The filtrate was brought to *p*H 6 with 4*N* sodium hydroxide and the solid (404 mg) was recrystallized from the minimum amount of methanol to give more thiol (160 mg), mp 167-170°. The overall yield was 54.8%. The analytical sample had mp 169-170° (from absolute ethanol); ir (potassium bromide): 2600 (⁺NH), 1520, 1350 cm^{-1} (NO_2); nmr (deuteriochloroform): δ 8.8 (d, 1H, $J_{4,5}$ = 5 Hz, H_4), 8.48 (d, 1H, J_{BC} = 2.2 Hz, H_C), 8.3-7.65 (m, 4H, H_6, H_3, H_A, H_B),7.5-7.3 (m, 1H, H_5); ms: m/e 232 ($M^{\cdot}$), 231 ($M^{\cdot}$-H), 216 ($M^{\cdot}$-O), 186 ($M^{\cdot}$-H-NO_2).

Anal. Calcd. for $C_{11}H_8N_2O_2S$: C, 56.90; H, 3.45. Found: C, 57.05; H, 3.50.

Treatment of **7** (230 mg) with excess 48-50% tetrafluoroboric acid solution gave **7** tetrafluoroborate (256 mg, 50%), mp 179-181° (from nitromethane), depressed on admixture with **7**; ir (potassium bromide): 2800-2600 (br) (⁺NH), 1520, 1350 (NO_2), 1050 cm^{-1}(BF_4^-).

Anal. Calcd. for $C_{11}H_9BF_4N_2O_2S.H_2O$: C, 39.07; H, 3.29. Found: C, 39.05; H, 3.27.

(b) From the *O*-arylthiocarbamate (**8**).

O-[2-(2-Pyridyl)-4-nitrophenyl]dimethylthiocarbamate (0.606 g) was heated at 180° under dry nitrogen for 1 hour. A solution of potasium hydroxide (0.4 g) in water (1 ml) and ethylene glycol (5 ml) was added and the mixture heated under reflux for 1 hour. The cooled solution was poured into ice (20 g) and the mixture extracted with chloroform (2 × 20 ml). The extracts were discarded and the aqueous layer made just acid with hydrochloric acid and extracted with chloroform (3 × 20 ml). The dried (magnesium sulfate) extract was evaporated to give the thiol (0.093 g, 20%), mp 169-170° (from ethanol). Using procedure (b) above (without purification of the intermediate *S*-arylthiocarbamate) but using acid hydrolysis as in (a) rather than base hydrolysis as in (b), the folllowing thiols were prepared:

2-(3-Cyano-2-mercaptophenyl)pyridine.

This compound was obtained in a yield of 13.4%, mp 208-208.5°.

Anal. Calcd. for $C_{12}H_8N_2S$: C, 67.89; H, 3.91. Found: C, 67.87; H, 3.81.

2-(5-Cyano-2-mercaptophenyl)pyridine (**11**).

This compound was obtained in a yield of 63.7%, mp 222-223°.

Anal. Calcd. for $C_{12}H_8N_2S$: C, 67.89; H, 3.81. Found: C, 67.90; H, 3.82.

7-Nitrobenzisothiazolo[2,3-*a*]pyridinium Tetrafluoroborate (**4**, X = NO_2).

To a suspension of *N*-chlorosuccinimide (172 mg) in dry benzene (10 ml) at 0-10° under dry nitrogen was added a suspension of 2-(2-mercapto-5-nitrophenyl)pyridine (**7**) (300 mg) in dry benzene (5 ml) over a 15 minute period in the absence of light. The suspension was stirred and its temperature kept 10° for another 20 minutes. A solution of silver tetrafluoroborate (251 mg) in dry acetonitrile (5 ml) was added and the mixture stirred at room temperature for 1 hour. The yellow precipitate was filtered and washed with ether. It was boiled with methanol (20 ml), filtered from silver chloride, and the solution evaporated. The residue was recrystallized from chloroform to give **4** (X = NO_2) (245 mg, 60%), mp 230-235° dec; ir (potassium bromide): ir 1530, 1350 (NO_2), 1050 cm^{-1} (BF_4^-); nmr (DMSO-d_6) δ 10.0 (d, 1H, H_6), 9.75 (s, 1H, H_C), 9.5 (d, 1H, H_5), 8.9-8.5 (m, 3H, H_3, H_4, H_B), 8.2 (t, 1H, H_A).

Anal. Calcd. for $C_{11}H_7BF_4N_2O_2S$: C, 41.54; H, 2.22; N, 8.81. Found: C, 41.54; H, 2.26; N, 8.82.

7-Cyanobenzisothiazolo[2,3-*a*]pyridinium Tetrafluoroborate (**4**, X = CN).

This was prepared similarly from **11** and obtained in 56.5% yield, mp 246-251° dec.

Anal. Calcd. for $C_{12}H_7BF_4N_2S$: C, 48.35; H, 2.37. Found: C, 48.54; H, 2.44.

Reaction of **4** (X = NO_2) with HMPA and with Sodium Azide.

The pyridinium salt (128 mg) and hexamethylphosphorus triamide (2 ml) were heated at 120-125° under dry nitrogen for 1 hour. The cooled

solution was treated with water (10 ml) to give 2-(2-mercapto-5-nitrophenyl)pyridine (**7**) (46 mg, 50%), identical (mp and ir) with authentic material.

A similar result was obtained when **4** (X = NO_2) was heated with a solution of sodium azide in acetonitrile, **7** (78.5%) was obtained.

Reaction of **4** (X = NO_2) with Sodium Hydroxide.

The pyridinium salt (416 mg) in water (14 ml) under oxygen-free nitrogen was treated with a 2% aqueous solution of sodium hydroxide (5.4 ml) at room temperature over a period of 20 minutes. A deep, cranberry-red color formed immediately but gradually turned light yellow. The mixture was stirred for a further 40 minutes, adjusted to *p*H 6 with concentrated hydrochloric acid and the precipitated **7** (194 mg, 64%) filtered. It was identical with an authentic sample. The filtrate was concentrated *in vacuo* at room temperature to give a yellow solid which was purified by tlc on silica gel using acetone-methanol (8:2 v/v) as the developer. The zone with R_f 0.1 was extracted to give a solid (60 mg) which was treated with dry methanol (2 ml), filtered, and the filtrate evaporated to give a yellow solid (11 mg), mp 205-210° dec; ir (potassium bromide): 3450-3200 (br), 1515, 1345 cm^{-1}. A pure material could not be obtained.

Anal. Calcd. for $C_{11}H_8N_2O_4S$: C, 49.99; H, 3.06. Calcd. for $C_{11}H_7N_2NaO_4S$: C, 46.15; H, 2.44. Found: C, 35.40; H, 2.59.

3-Bromo-1-(*p*-nitrophenoxy)pyridinium Tetrafluoroborate (**5**; R = Br, X = NO_2) (with S. Kato).

A solution of *p*-nitrobenzenediazonium tetrafluoroborate (7.11 g) and 3-bromopyridine 1-oxide (5.22 g) in acetonitrile (80 ml) was stirred at room temperature for 12 hours and then heated under reflux for 8 hours. The solvent was evaporated and the residue recrystallized from methanol to give the pyridinium salt (7.08 g, 60%), mp 155-156°; nmr (DMSO-d_6): δ 9.74 (s, 1H, H_2), 9.24 (d, 1H, $J_{5,6}$ = 7 Hz, H_6), 8.62 (d, 1H, $J_{4,5}$ = 8 Hz, H_4), 7.87 (q, 1H, $J_{4,5}$ = 8 Hz, $J_{5,6}$ = 7 Hz, H_5) 7.85 (d, 2H, J_{AB} = 9 Hz, H_B), 7.0 (d, 2H, J_{AB} = 9 Hz, H_A).

Anal. Calcd. for $C_{11}H_8BBrF_4N_2O_3$: C, 34.50; H, 2.09. Found: C, 34.47; H, 2.14.

3-Fluoro-1-(*p*-nitrophenoxy)pyridinium Tetrafluoroborate (**5**, R = F, X = NO_2).

This was prepared similarly and obtained in 54% yield, mp 133-136° (from CH_3CN); ms: m/e (M^+-2HF), 252 (M^+-2HF-NO), 235 (M^+-BF_4^-). The molecule retained some acetonitrile of crystallization.

Anal. Calcd. for $C_{11}H_8BF_5N_2O_3.1/5CH_3CN$: C, 41.45; H, 2.63. Found: C, 41.63; H, 2.54.

3-Bromo-2-(2-hydroxy-5-nitrophenyl)pyridine (**6**, R = Br, R′ = H, X = NO_2).

A solution of 3-bromo-1-(*p*-nitrophenoxy)pyridinium tetrafluoroborate (2.30 g) and potassium phenoxide (0.96 g) in acetonitrile (50 ml) was heated under reflux for 4 hours. The solvent was evaporated to dryness and the residue was treated with 2*N* hydrochloric acid (30 ml). Extraction with chloroform (3 × 40 ml) and evaporation of the dried (magnesium sulfate) extracts gave a residue (1.47 g) which was chromatographed on a column of silica gel (2.4 × 24 cm). Elution with light petroleum (bp 30-60°)-benzene (1:1 v/v) gave 5-bromo-2-(2-hydroxy-5-nitrophenyl)-pyridine (4 mg, <1%), mp 225° (ethanol); ir (potassium bromide): 2600 (-$^+$NH=), 1520, 1350 cm^{-1} (NO_2); nmr (deuteriochloroform): δ 9.00 (d, 1H, $J_{4,6}$ = 2 Hz, H_6), 8.80 (m, 2H, H_4 and H_C), 8.45 (m, 2H, H_3 and H_B), 7.34 (d, 1H, J_{AB} = 9 Hz, H_A); ms: m/e 296, 294 (M^+), 266, 264 (M^+-NO), 250, 248 (M^+-NO_2).

Anal. Calcd. for $C_{11}H_7BrN_2O_3$: C, 44.75; H, 2.38. Found: C, 44.80; H, 2.47.

Elution with benzene (300 ml) yielded 3-bromo-3-(2-hydroxy-5-nitrophenyl)pyridine (1.06 g, 60%), mp 165° (ethanol); ir (potassium bromide): 2600 (-$^+$HN=), 1520, 1350 cm^{-1} (NO_2); nmr (deuteriochloroform) δ 9.24 (d, 1H, J_{BC} = 3 Hz, H_C), 8.52 (dd, 1H, $J_{5,6}$ = 5.5 Hz, $J_{4,6}$ = 1.6 Hz, H_6), 8.17 (dd, 1H, J_{AB} = 9 Hz, J_{BC} = 3 Hz, H_B), 8.10 (dd, 1H, $J_{4,6}$ = 1.6 Hz, $J_{4,5}$ = 7 Hz, H_4), 7.22 (dd, 1H, $J_{4,5}$ = 7 Hz, $J_{4,6}$ = 5.5 Hz, H_5), 7.05 (d, 1H, J_{AB} = 9 Hz, H_A); ms: m/e 296, 294 (M^+) 280, 278 (M^+-O), 266, 264 (M^+-NO), 250 (M^+-NO), 250 (M^+-NO_2), 222,220 (M^+-NO_2-CO).

Anal. Calcd. for $C_{11}H_7BrN_2O_3$: C, 44.75; H, 2.38. Found: C, 44.69; H, 2.44.

O-[2-(3-Bromo-2-pyridyl)-4-nitrophenyl]dimethylthiocarbamate (**18**).

This was prepared as were **8** above from the phenol (3.25 g), sodium hydroxide (0.44 g) and dimethylthiocarbamoyl chloride (2.74 g): 2.66 g (63.5%), mp 111.5-113° (from ether); ir (Nujol): 1520 (C=S), 1510, 1345 cm^{-1} (NO_2).

Anal. Calcd. for $C_{13}H_{12}BrN_3O_3S$: C, 43.99; H, 3.18. Found: C, 43.90; H, 3.20.

7-Nitrobenzothiopheno[3,2-*b*]pyridine (**19**).

The thiocarbamate (**18**) (2.66 g) was heated under nitrogen for 1 hour at 190-195°. A solution of potassium hydroxide (1.46 g) in water (4 ml) and ethylene glycol (18 ml) was then added and the solution heated under reflux for 45 minutes. On cooling the solution, 7-nitrobenzothiopheno-[3,2-*b*]pyridine separated (1.57 g, 98%), mp 258-260°; ir (Nujol): 1510, 1340 cm^{-1} (NO_2); ms: m/e (relative intensity) 232 (8) (M^++2), 231 (19) (M^++1), 230 (100) (M^+), 200 (27) (M^+-NO), 184 (99) (M^+-NO_2).

Anal. Calcd. for $C_{11}H_6N_2O_2S$: C, 57.39; H, 2.63. Found: C, 57.37; H, 2.63.

7-Aminobenzothiopheno[3,2-*b*]pyridine (**20**).

The nitro compound (**19**) (0.10 g) was added to a solution of stannous chloride (0.6 g) in 6*N* hydrochloric acid (6 ml) and the solution was boiled under reflux for 3.5 hours. It was brought to *p*H 10 with 30% aqueous sodium hydroxide and extracted with ether (4 × 10 ml). The dried magnesium sulfate extracts were evaporated to give the amine (**20**) (60 mg, 69%), mp 186-187° (from ethanol): ir (Nujol): 3300-3200 (br) cm^{-1} (NH_2); nmr (deuteriochloroform): δ 8.68 (dd, 1H, $J_{2,3}$ = 4.2 Hz, $J_{2,4}$ = 1.1 Hz, H_2), 8.10 (dd, 1H, $J_{3,4}$ = 6.7 Hz, $J_{2,4}$ = 1.1 Hz, H_4), 7.80-7.20 (m, 3H, H_3, H_5, H_8), 6.90 (dd, 1H, $J_{5,6}$ = 8.4 Hz, $J_{6,8}$ = 1.7 Hz, H_6), 3.7 (s, 2H, NH_2, exchangeable); ms: m/e (relative intensity) 203 (4), 202 (34) (M^++2), 201 (91) (M^++1), 200 (100) (M^+).

Anal. Calcd. for $C_{11}H_8N_2S$: C, 65.99; H, 4.04. Found: C, 65.97; H, 4.05. (Calcd. for $C_{11}H_{10}N_2S$ (202): C, 65.33; H, 4.99).

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(11) The facile formation of **7** from these reactions initially suggested that **12** had *not* given **4** (X = NO_2) but that, instead, it had undergone hydrolysis to give the pyridinium tetrafluoroborate salt of **7** on treatment with silver tetrafluoroborate. An authentic sample of this tetrafluoroborate was prepared from **7** and aqueous tetrafluoroboric acid. The product proved to be completely different from **4**, thus confirming the proposed structure for the latter.