melting at 203–205° (sealed) after several recrystallizations from hexane or ethanol–benzene. The per cent homoannularity value[6] was 104. A less stable modification (X-ray diffractogram: 5.74, 4.99, 6.28, 3.64, and 4.26) with melting point in the same range was occasionally obtained by quickly cooling a concentrated solution or quenching the melt of the compound. The latter modification, which frequently prevailed in the presence of major portions of IIb or IIc as contaminants, could be reconverted to the more stable form by allowing it to crystallize slowly from its solutions.

1,3-Bis(ferrocenylmethyl)ferrocene (IIb), orange-yellow crystals, m.p. 146–147° (from hexane or ethanol), occurred as a predominant modification (X-ray diffractogram: 5.78, 5.30, 4.55, 3.88, and 3.46), with a per cent homoannularity of 97. This form was converted by fusing and quenching (and also by quickly chilling concentrated isopropanol–benzene solutions) into a second modification, m.p.[18] 145–147°, similar in X-ray peak positions and relative intensities [X-ray diffractogram: 5.75, 5.05 (6.28 missing), 3.62, and 4.26] to the less stable one of IIa. The per cent homoannularity value was 94. Reconversion to the predominant modification was accomplished by slow recrystallization from isopropanol–benzene.

1,1′-Bis(ferrocenylmethyl)ferrocene (IIc) occurred as a stable modification (X-ray diffractogram: 5.44–5.53 (doublet), 5.25, 5.05, 4.37, and 4.72) and occasionally as a second modification (X-ray diffractogram: 4.90, 5.62, 5.88, 4.13, and 3.96), both in the form of fluffy, yellow needles melting at 164–166° (no depression on admixture of authentic compound prepared as described elsewhere[7]) and giving per cent homoannularity values in the same range (average from four determinations, 69.1). Again, the second modification could be retransformed to the more stable one by slow crystallization from isopropanol–benzene.

All modifications of the three isomers were repeatedly analyzed for C, H, and Fe and molecular weight in various stages of fractionation. In all instances, values identical within the experimental error limit were obtained. Typical findings on the pure compounds are recorded in Table II.

Isomers IIIa–c.—All operations in the following Friedel–Crafts procedure were conducted under dry nitrogen, and the solvents were predried in the usual manner. To 1.80 g. (7.8 mmoles) of ferrocenecarboxylic acid (m.p. 205–215°, Metallomer Laboratories, Fitchburg, Mass.) in 100 ml. of benzene was added slowly 1.66 g. (8.0 mmoles) of phosphorus pentachloride. The mixture was stirred for 25 min. at room temperature, and the solvent was replaced by an equal volume of methylene chloride. To this stirred suspension of the acid chloride was added 1.04 g. (7.8 mmoles) of anhydrous aluminum chloride, and the resulting purple solution was added dropwise, over a 1-hr. period, to the ice-cold solution of 3.10 g. (8.1 mmoles) of diferrocenylmethane (m.p. 143–145°, prepared as described[2a]) in 160 ml. of methylene chloride. After stirring for 30 min. at room temperature and another 30 min. at reflux, the mixture was hydrolyzed in the presence of reducing agent (sodium bisulfite) and worked up further in the conventional manner, to give 4.25 g. of crystalline material obtained from the organic phase.

Chromatography of this crude mixture on alumina (Merck, activity I), with ether as eluent (3-day elution time), yielded three distinct zones. Unreacted diferrocenylmethane (1.80 g.) was recovered from the first band,[19] while the second band furnished 0.278 g. (6.0%) of 1-ferrocenoyl-2-ferrocenylmethylferrocene (IIIa), salmon red crystals, m.p. 176–178° (cyclohexane). The third, very broad band, containing IIIb and IIIc, was eluted in several cuts. From the first portion, crude 1,1′ isomer IIIc was isolated; fractional crystallization from cyclohexane yielded 0.275 g. (5.9%) of product, m.p. 157–159°, per cent homoannularity 73.0. The tail portion of the same band (no further separation of the center portion was attempted) similarly afforded crude 1,3 isomer IIIb, m.p. 180–197°. Further purification of this compound by fractional crystallization from cyclohexane gave 0.215 g. (4.6%) of material exhibiting the constant m.p. 212–214° (sealed). All analytical data and molecular weight values for the three isomers are recorded in Table II.

Compound IIIa, 50 mg., was subjected to a Clemmensen reduction by amalgamated zinc (60 mg.) in refluxing ethanol–benzene (3 hr.) in the conventional manner, followed by chromatography in hexane on alumina (Alcoa, F-20, exposed for 6 hr. to air of 40% relative humidity). Elution with hexane produced a single yellow band which afforded 30 mg. of crude 1,2-bis(ferrocenylmethyl)ferrocene. After recrystallization from isopropanol–benzene, the compound had m.p. 202–204° and was identical in infrared spectrum and X-ray diffractogram with IIa reported above (no melting point depression on a mixed sample). Analogously, IIIb and IIIc were reduced to give, respectively, 36 mg. of crude IIb (m.p. 147°) and 29 mg. of crude IIc (m.p. 163–165°) (both on recrystallized samples), with identification in these cases again confirmed by mixture melting point and comparison of infrared and X-ray patterns.

(18) Occasionally, this modification was found to melt at 90–94°, resolidifying upon further temperature rise, and remelt in the 140–145° range.

(19) In one instance, the trailing portion of this band contained a second compound, m.p. 172–174°, identical with diferrocenylcarbinol [K. Schlögl and A. Mohar, *Monatsh. Chem.*, **92**, 219 (1961); R. L. Schaaf, *J. Org. Chem.*, **27**, 107 (1962)]; no melting point depression on admixture of an authentic sample kindly provided by Dr. Schaaf. This product probably arose from autoxidation of diferrocenylmethane on the column.

2-Aminobenzo[*b*]thiophene. An Aromatic Ring Tautomer[1,2]

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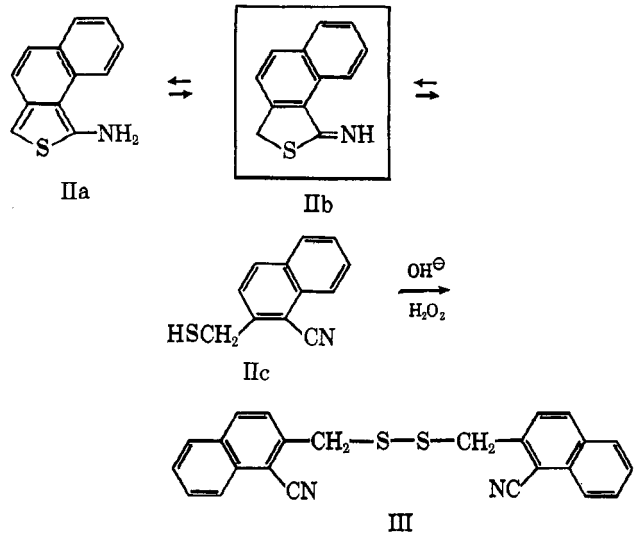
Synthesis of 2-aminobenzo[*b*]thiophene (I), a representative of an elusive group of thiophene derivatives, has been achieved in a five-step sequence from thiosalicylic acid (IV) in a 48% over-all yield. Prior to this, primary aminothiophenes and aminobenzothiophenes have frequently been regarded inisolable as pure, free bases. The key step of the synthesis is the aluminum bromide cleavage of the benzyl sulfide VIII to give 80% of I; this little-known procedure appears to have superior potential in the synthesis of sulfur heterocycles. The structure of I is clearly established by spectroscopic evidence, including an examination of the partially deuterated derivative. Chemically, I has the expected properties of a heterocyclic amine. It may be diazotized and subsequently converted to the 2-bromo or 2-ketodihydro derivatives, respectively (XIII, XVb). Unlike naphtho[1,2-*c*]thiophene-1(3H)-imine (II), I resists ring opening and subsequent oxidation to a disulfide (XVI). Thus, Ia may be defined as an "aromatic ring tautomer" of Ic, stable and incapable of displaying chain tautomerism.

Recently we have found that the tautomeric system II in the crystalline state or in neutral or acidic solution exists as naphtho[1,2-*c*]thiophene-1(3H)-imine (IIb).[2,3] However, alkaline conditions permit this substance to behave as the chain tautomer IIc. For

(1) (a) Presented on sabbatical leave (G. W. S.) at various universities in Australia and New Zealand, 1963, and before the Division of Organic Chemistry at the 149th Meeting of the American Chemical Society, Detroit, Mich., April 1965; *Chem. Eng. News*, **43**, 16, 45 (1965). (b) In part from the M.S. Thesis of F. W. Villaescusa, Washington State University, Feb. 1963. (c) N.S.F. Summer Fellow, 1963; N.S.F. Cooperative Fellow, 1963–1964. (d) In part from the Ph.D. Thesis of T. E. Wollner, Washington State University, June 1965.

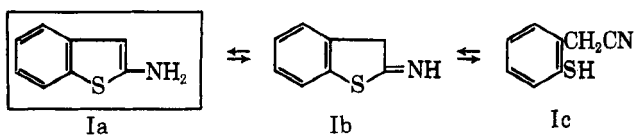
(2) For paper I on tautomerism, see G. W. Stacy, A. J. Papa, F. W. Villaescusa, and S. C. Ray, *J. Org. Chem.*, **29**, 607 (1964).

(3) An enclosure around the structure denotes the stable tautomer.



example, II is cleanly oxidized by alkaline hydrogen peroxide to the disulfide III.

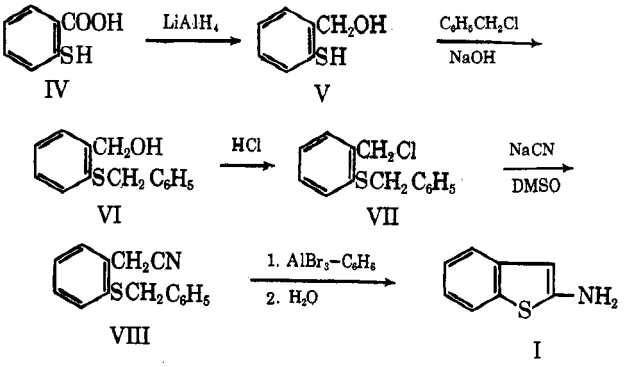
In view of this, it was now of interest to examine the tautomeric system I, where presumably 2-aminobenzo[*b*]thiophene (Ia) would be the stable form. This was anticipated, for, unlike IIa (*o*-quinoidal structure), aromatic stability would not be disrupted by the structural requirements of the amino tautomer but on the contrary be reinforced. If this speculation were correct, it then would be of interest to ascertain if such an aromatic ring tautomer would exhibit chain tautom-



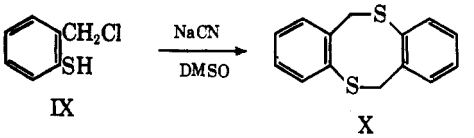
erism, as does II. Of equal interest was a comparison of spectral properties of I with II, as previously described.

Actually, the synthesis of 2-aminobenzo[*b*]thiophene (Ia) in itself presented a challenge, as, surprisingly, it had not been previously reported. Two factors might be offered in explanation. Firstly, benzo[*b*]-thiophene itself substitutes preferentially in the 3-position.[4] Direct nitration, therefore, would result in 3-nitrobenzo[*b*]thiophene as the precursor for the 3-amino derivative.[5] Secondly, and more significantly, aminothiophenes are well known for their instability.[6] Indeed, this problem has been sufficiently frustrating that the synthesis of tertiary aminothiophenes has recently been studied and the resulting free bases have been found stable.[7] In the benzo[*b*]thiophene series itself, 3-aminobenzo[*b*]thiophene[5] and the 2(3)-amino-3(2)-methylbenzo[*b*]thiophenes have been isolated only as acetyl derivatives.[8]

It is clear from this background that a synthesis of Ia was a discouraging prospect. Nevertheless, we now are able to announce the achievement of this objective. The synthesis was carried out in five steps



in an over-all yield of 48% from thiosalicylic acid (IV). The key reaction involves the little-known but excellent thio ether cleavage of Harnish and Tarbell.[9] By this procedure, we were able to obtain I as a stable, crystalline solid in 80% yield. The reaction apparently involves complexing with aluminum bromide, disproportionation to form benzyl bromide and a bromoaluminum salt of I, and finally hydrolysis of this salt and ring closure to yield Ia. This procedure for removal of a protecting benzyl group from sulfur, as in this case, should in many other instances surpass the classical method employing sodium–liquid ammonia and constitute a useful device in the synthesis of sulfur heterocycles. In the initial step, reduction of thiosalicylic acid (IV) with lithium aluminum hydride was prompted by a similar reduction of salicylic acid and proceeded quantitatively.[10] The subsequent benzylation of sulfur in V was also quantitative and involved no complications in respect to the hydroxyl group. Maximum over-all yields were obtained by using crude intermediates in the case of V and VI. Apparently, their use in no way adversely affected these reactions. Displacement of the hydroxyl group of VI and the chloro group of VII was accomplished in good yield in both cases. It should be pointed out, however, that attempted conversion of the intermediate IX to the nitrile Ic did not succeed. Under a variety of conditions mainly polymeric material resulted; however, sublimation of the crude product produced a small amount of the previously unreported 6H,12H-dibenzo[*b*,*f*][1,5]dithiocin (X). Under conditions of high dilution, X was obtained in larger yield.



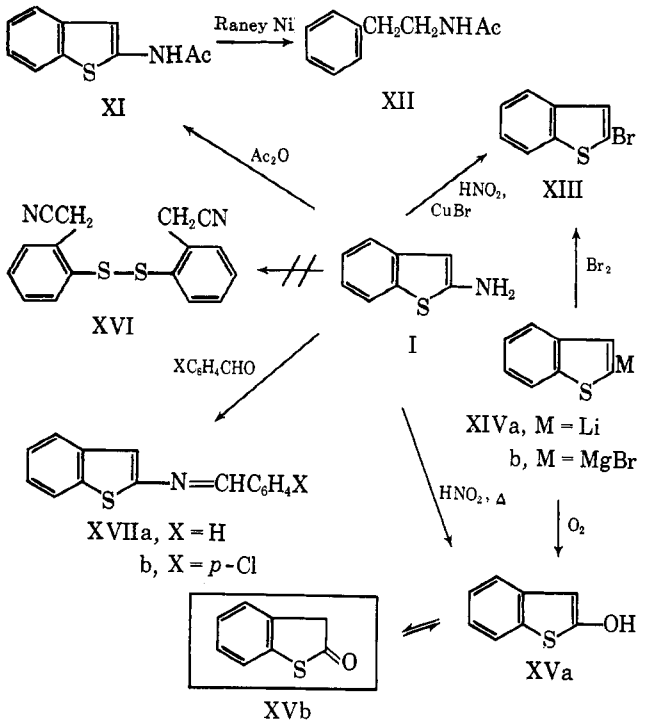
Masking the thiol group of IX by conversion to its corresponding disulfide also failed in an attempted introduction of the nitrile group.

Spectroscopic evidence established the structure of I as the stable ring tautomer, 2-aminobenzo[*b*]thiophene (Ia). The infrared spectrum did not contain the characteristic peaks for imino (Ib) or nitrile (Ic) groups but did have peaks for the N–H stretching frequency at 3400 and 3300 cm.$^{-1}$, for a primary amine. After partial deuteration of I, the infrared spectrum contained three new bands at 2450, 2520, and 2580 cm.$^{-1}$ and a weak band at 3390 cm.$^{-1}$. The absorptions at 2450 and 2580 cm.$^{-1}$ correspond to the

(4) D. A. Shirley and M. D. Cameron, *J. Am. Chem. Soc.*, **74**, 664 (1952).
(5) K. Fries and E. Hemmecke, *Ann.*, **470**, 1 (1929).
(6) (a) E. Campaigne and P. A. Monroe, *J. Am. Chem. Soc.*, **76**, 2447 (1954); (b) W. Steinkopf, *Ann.*, **403**, 17 (1914).
(7) (a) F. A. Buiter, J. H. Sperna Weiland, and H. Wynberg, *Rec. trav. chim.*, **83**, 1160 (1964); (b) J. B. Sullivan and W. C. McCarthy, *J. Org. Chem.*, **30**, 662 (1965).
(8) D. A. Shirley, M. J. Danzig, and F. C. Canter, *J. Am. Chem. Soc.*, **75**, 3278 (1953).
(9) D. P. Harnish and D. S. Tarbell, *ibid.*, **70**, 4123 (1948).
(10) R. F. Nystron and W. G. Brown, *ibid.*, **69**, 2548 (1947).

symmetric and asymmetric stretching modes for the $-ND_2$ group, while the weaker band at 2520 cm.$^{-1}$ may be assigned to the N–D stretching frequency for the –NHD group.[11] The single weak band at 3390 cm.$^{-1}$ is due to the N–H stretch of the –NHD group. The ultraviolet spectrum showed an absorption maximum at 281 mμ compared with 288 mμ for the parent benzo[*b*]thiophene. The n.m.r. spectrum was equally compelling showing a chemical shift for the proton of the 3 position at δ 6.19, a broad peak for the aromatic amino group at 3.89, and a multiplet corresponding to the benzene ring at 7.1–7.8 in an area ratio of 1:2:4. These facts clearly supported the amino tautomer Ia and ruled out the imino form Ib.

The chemical behavior of I was consistent with that of an aromatic heterocyclic amine. An acetyl derivative XI shows a strong N–H stretching band in the



infrared spectrum, and its n.m.r. spectrum was in accord with the single proton in position 3 of the benzothiophene nucleus, evidence ruling out an acetyl*imino* group. Further, XI underwent desulfurization with Raney nickel to yield β-phenethylacetamide (XII). A simultaneous reduction of the point of unsaturation in the thiophene ring of XI during desulfurization is in agreement with prior work.[8,12] Schiff base formation (XVIIa, b), a reaction often considered characteristic of an amino group,[13] readily occurred by heating I with an appropriate aromatic aldehyde in ethanol.

It has been reported that 2-aminothiophene stannic chloride double salt may be diazotized, and that the resulting diazonium salt coupled normally with 2-naphthol.[14] Although in our case the coupling did not succeed, it was possible to replace the diazonium group of I by bromine. The resulting 2-bromobenzo[*b*]thiophene (XIII) was identical with a sample prepared by treating 2-thianaphthenyllithium (XIVa) with bromine.[4] The diazonium group was also displaced by a hydroxyl group when the acidic solution was heated to give 2-keto-2,3-dihydrobenzo[*b*]thiophene (XVb). This substance had been previously synthesized by air oxidation of 2-thianaphthenylmagnesium bromide and described as the enolic tautomer, benzo[*b*]thiophen-2-ol (XVa).[15] However, XV prepared by either method in our hands gave an identical keto tautomer XVb. This was substantiated by like infrared spectra, which showed no band corresponding to an O–H stretching frequency but one at 1700 cm.$^{-1}$ for a thiolactone carbonyl. Actually, XV could be formed by a direct acidic hydrolysis of I through heating for 3 days with 6 *N* hydrochloric acid in tetrahydrofuran. Where a tautomerically stable carbonyl will result in heterocyclic systems, an amino group frequently may be displaced in this way, as in the conversion of 5-dimethylaminoacridine to acridone.[16]

One of the objectives of this undertaking had been to investigate possible chain tautomerism of I under alkaline conditions. It was found that, unlike II, ring opening did not occur. As an example of one of several experiments, the attempted hydrogen peroxide oxidation to the disulfide (I → XVI compared with II → III) failed. Such stability identifies the 2-aminobenzo[*b*]thiophene (I) as an aromatic ring tautomer, apparently incapable of displaying chain tautomerism to Ic.

The observation that I exists as the amino tautomer Ia rather than the imino form Ib is in agreement with the recent findings of Gronowitz and Hoffman for 2-aminothiophene[17] and Dudek, *et al.*,[18] who have established in several cases of enamine–imine tautomerism that the enamine invariably is the stable tautomer.

Investigation of similar syntheses of other aminothiophenes and related heterocycles is being pursued.

Experimental Section

All melting points are corrected. Boiling points at reduced pressures are uncorrected. The microanalytical work was performed by the Galbraith Laboratories, Knoxville, Tenn. The infrared spectra were determined on Beckman IR-5 or IR-8 spectraphotometers and assignments were based on data cited by Bellamy,[19] if not otherwise stated. The spectra of liquids were run as neat films with sodium chloride optics. N.m.r. spectra were determined by a Varian A-60 spectrometer using carbon tetrachloride or deuterated chloroform as the solvent and tetramethylsilane as the internal standard. All chemical shifts are reported in δ units relative to tetramethylsilane taken at zero.

o-Mercaptobenzyl Alcohol (V).—A solution of 109 g. (0.71 mole) of thiosalicylic acid (IV) in 2 l. of anhydrous ether was added dropwise to a stirred suspension of 50 g. (1.3 moles) of lithium aluminum hydride in 600 ml. of ether (under nitrogen). After addition and stirring for 1 hr., the mixture was cooled, and 250 ml. of water was carefully added. Then 1 l. of 10% sulfuric acid was added dropwise, and the resulting mixture was stirred overnight. After ether extraction and drying over calcium chloride, the ether was removed to give a quantitative yield of crude *o*-mercaptobenzyl alcohol as a reddish brown

(11) (a) A. J. Boulton and A. R. Katritzky, *Tetrahedron*, **12**, 51 (1961); (b) H. M. Randall, N. Fuson, R. G. Fowler, and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1959, p. 43.

(12) H. Hauptmann and W. F. Walter, *Chem. Rev.*, **62**, 347 (1962).

(13) S. J. Angyal and C. L. Angyal, *J. Chem. Soc.*, 1461 (1952).

(14) N. I. Putokhin and V. I. Yakovlev, *Dokl. Akad. Nauk SSSR*, **98**, 89 (1954); *Chem. Abstr.*, **49**, 12341 (1955).

(15) G. van Zyl, D. C. DeJongh, V. L. Heasley, and J. W. van Dyke, *J. Org. Chem.*, **26**, 4946 (1961). Although these authors briefly mention a "keto form" in the Experimental section, their discussion describes this substance as "2-hydroxythianaphthene"; no structural evidence was presented.

(16) A. Albert and B. Ritchie, *J. Chem. Soc.*, 458 (1943).

(17) S. Gronowitz and R. A. Hoffman, *Arkiv Kemi*, **15**, 499 (1960).

(18) G. O. Dudek and G. P. Volpp, *J. Am. Chem. Soc.*, **85**, 2697 (1963).

(19) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

residue. An analytical sample was crystallized from pentane as long, colorless needles: m.p. 31–32°; $\nu_{max}^{10\%\ CHCl_3}$ (cm.$^{-1}$) 3400 (s), 3570 (s) (O–H), 2550 (w) (S–H).

Anal. Calcd. for C_7H_8OS: C, 59.96; H, 5.75; S, 22.87. Found: C, 59.90; H, 5.64; S, 23.01.

By reaction with 3.41 g. (0.024 mole) of benzoyl chloride, 1.40 g. (0.01 mole) of V in 7 ml. of anhydrous pyridine yielded a **2-thiobenzoate-1-benzyl benzoate**, which on recrystallization from methanol (Norit) gave 2.41 g. (69%) of pale yellow crystals, m.p. 88–90°.

Anal. Calcd. for $C_{21}H_{16}O_3S$: C, 72.39; H, 4.63; S, 9.20. Found: C, 72.41; H, 4.62; S, 9.25.

***o*-Benzylmercaptobenzyl Alcohol (VI).**—To a stirred solution (under nitrogen) of 31.2 g. (0.78 mole) of sodium hydroxide in 27 ml. of water and 320 ml. of 95% ethanol was added dropwise 98.0 g. (0.70 mole) of crude V. This mixture was stirred 0.5 hr., and 91.0 g. (0.72 mole) of benzyl chloride was added dropwise with cooling. After the addition, the mixture was heated under reflux for 5 hr. and then was stirred at room temperature overnight. After sodium chloride was filtered off, the ethanol was distilled. The residue was extracted with ether, and the extract was washed with water, with 5% sodium hydroxide, and again with water and was dried over sodium sulfate. Removal of the ether gave a quantitative yield of VI as a crude, brown solid.

An analytical sample was prepared by the recrystallization of 2.00 g. from petroleum ether (b.p. 30–60°) to afford long, colorless needles, m.p. 48.5–49.5°, $\nu_{max}^{10\%\ CCl_4}$ (cm.$^{-1}$) 3400 (s) (O–H).

Anal. Calcd. for $C_{14}H_{14}OS$: C, 73.01; H, 6.13; S, 13.92. Found: C, 73.12; H, 5.98; S, 14.02.

***o*-Benzylmercaptobenzyl Chloride (VII).**—A mixture of 22.0 g. (0.088 mole) of crude VI and 165 ml. of concentrated hydrochloric acid was heated at 55° for 19 hr. After the mixture was cooled and the oil was separated, the aqueous phase was diluted with 100 ml. of water and was extracted with ether. After a standard work-up, the residual oil was vacuum distilled to yield 18.0 g. (78%) of VII, b.p. 140–142° (0.1 mm.), $n^{25}D$ 1.6228, d^{20}_4 1.223.

Anal. Calcd. for $C_{14}H_{13}ClS$: C, 67.59; H, 5.26; Cl, 14.25. Found: C, 67.37; H, 5.29; Cl, 14.16.

***o*-Benzylmercaptophenylacetonitrile (VIII).**—A procedure similar to that of Smiley and Arnold was applied.[20] By stirring at 75°, 14.7 g. (0.30 mole) of sodium cyanide was dissolved in 150 ml. of dimethyl sulfoxide.[21] To this solution was added 61.0 g. (0.24 mole) of VII over a period of 20 min. with the temperature maintained at 88° for 4.5 hr. The reaction mixture was then cooled and was poured with vigorous stirring into 100 g. of ice in 500 ml. of water. Subsequently, the residue was distilled to give 45.0 g. (78%) of VIII as a yellow oil, b.p. 140–142° (0.06 mm.). For analysis, a sample was crystallized from 95% ethanol (Norit) to give colorless crystals, m.p. 43.5–44°, $\nu_{max}^{10\%\ CCl_4}$ (cm.$^{-1}$) 2250 (m) (C≡N).

Anal. Calcd. for $C_{15}H_{13}NS$: C, 75.28; H, 5.47; S, 13.40. Found: C, 75.08; H, 5.17; S, 13.14.

2-Aminobenzo[*b*]thiophene (I).—With some modification, the procedure of Harnish and Tarbell[9] was employed. To a cooled, stirred solution of 8.0 g. (0.03 mole) of anhydrous aluminum bromide in 30 ml. of benzene was added dropwise a solution of 5.0 g. (0.02 mole) of VIII in 10 ml. of benzene. The mixture was stirred (nitrogen) at room temperature for 48 hr. and was then cooled in an ice bath while 75 ml. of water was added dropwise. The resulting mixture was extracted with ether (three 40-ml. portions), and the combined ether extracts were washed with saturated sodium chloride solution (two 30-ml. portions) and dried over magnesium sulfate. After ether removal, the residual solid was crystallized from 25 ml. of carbon tetrachloride to yield 2.5 g. (80%) as long, colorless needles: m.p. 115–117°; $\nu_{max}^{10\%\ CCl_4}$ (cm.$^{-1}$) 3300 and 3400 (NH_2); n.m.r. spectrum, benzene ring 7.1–7.8, CH (3-position) 6.19, NH_2 3.89, area ratio 4:1:2. The ultraviolet absorption spectrum gave λ_{max}^{EtOH} 281 mμ (ε 9000) compared with that of the parent hydrocarbon, λ_{max}^{EtOH} 288 mμ (ε 2300).

Anal. Calcd. for C_8H_7NS: C, 64.39; H, 4.73; N, 9.39; S, 21.49. Found: C, 64.23; H, 4.73; N, 9.14; S, 21.26.

Treatment of an ethereal solution of I with anhydrous hydrogen chloride resulted in the separation of **2-aminobenzo[*b*]thiophene hydrochloride**. This compound had no well-defined melting point.

Anal. Calcd. for C_8H_8ClNS: C, 51.75; H, 4.34; Cl, 19.10; S, 17.27. Found: C, 51.59; H, 4.27; Cl, 19.37; S, 17.39.

A **phenylthioureide** was obtained from 150 mg. (1.0 mmole) of I and 135 mg. (1.0 mmole) of phenyl isothiocyanate in 1 ml. of absolute ethanol to give, after recrystallization from ethanol, 120 mg. (42%), m.p. 176–177°.

Anal. Calcd. for $C_{15}H_{12}N_2S_2$: C, 63.34; H, 4.26; S, 22.54. Found: C, 63.37; H, 4.49; S, 22.72.

2-Deuterioaminobenzo[*b*]thiophene.—To 0.20 g. of I was added 1 ml. of deuterium oxide and 3 ml. of dioxane (dried over calcium chloride). The flask was stoppered, wrapped in aluminum foil to exclude light and thus retard decomposition, and shaken intermittently for 1.5 hr. After removal of the major part of the solvent (40 mm.), the remaining traces were eliminated by lyophylization. Deuterium analysis of the partially deuterated I was obtained by integration of the peak areas of the n.m.r. spectrum.[22] The aromatic protons were employed as an internal standard, and the value cited for the deuterium constant is the average of three scans of the same sample. Thus, the value was found to be 49%: $\nu_{max}^{5\%\ CCl_4}$ (cm.$^{-1}$) 3390, 2520 (N–H and N–D from –NHD), 2580, 2450 (asym. and sym. N–D from $-ND_2$).

***o*-Mercaptobenzyl Chloride (IX).**—To 7.02 g. (0.05 mole) of V was added 30 ml. of concentrated hydrochloric acid, and the mixture was stirred at 45° for 14 hr., after which it was cooled and extracted with ether. After work-up, the residual oil was distilled (pot temperature 70°[23]) to yield a clear viscous liquid, 6.92 g. (87%), b.p. 40–41° (0.05 mm.), d^{20}_4 1.295, $n^{25}D$ 1.640, ν_{max} (cm.$^{-1}$) 2550 (m) (SH).

Anal. Calcd. for C_7H_7ClS: C, 53.00; H, 4.45; Cl, 22.35. Found: C, 53.05; H, 4.26; Cl, 22.23.

Bis(*o*-chloromethylphenyl) Disulfide.—To 8.27 g. (0.052 mole) of chloride IX at 50° was added 35 ml. of 35% hydrogen peroxide; the mixture was stirred at 50° for 20 hr. After cooling and extraction with ether, the extracts were dried over sodium sulfate. The ether was removed, and the sticky residue was extracted with five 100-ml. portions of petroleum ether (b.p. 30–60°) by heating the residue with each portion for 2 hr. The combined extracts were chilled at −15° overnight to afford 3.69 g. of crude disulfide. This was recrystallized from 400 ml of petroleum ether (Norit) to yield 3.02 g. (37%) pale yellow crystals, m.p. 47–50°, and, after additional recrystallization, m.p. 48.5–50.5°.

Anal. Calcd. for $C_{14}H_{12}Cl_2S_2$: C, 53.33; H, 3.84; Cl, 22.49. Found: C, 53.06; H, 3.71; Cl, 22.38.

Attempted Synthesis of I from *o*-Mercaptobenzyl Chloride (IX). 6H,12H-Dibenzo[*b*,*f*][1,5]dithiocin (X).—The general procedure was to dissolve or suspend the inorganic cyanide in the appropriate solvent, dilute the *o*-mercaptobenzyl chloride (IX) with solvent, and add it dropwise with stirring to the cyanide solution. It was then worked up by evaporation of the solvent or pouring the reaction mixture into water, extraction with ether, and removal of the ether. Various solvent and salt combinations were investigated (*e.g.*, sodium cyanide–dimethyl sulfoxide). Only semisolid, intractable products were obtained. Although these could not be recrystallized, sublimation (0.1 mm., 100°, 16 hr.) of the polymeric products yielded varying small amounts of 6H,12H-dibenzo[*b*,*f*][1,5]dithiocin (X), m.p. 174–176°.

Anal. Calcd. for $C_{14}H_{12}S_2$: C, 68.81; H, 4.95; S, 26.24; mol. wt., 244. Found: C, 68.64; H, 4.94; S, 26.36; mol. wt. (Rast camphor), 252.

The dithiocin X was prepared in higher yields by adding 2.02 g. (0.013 mole) of IX in 200 ml. of ethanol (4 hr.) to 5.0 g. of sodium hydroxide dissolved in 300 ml. of ethanol. After work-up, sublimation of the residue yielded 0.39 g. (25%), m.p. 171–174°.

2-Acetaminobenzo[*b*]thiophene (XI).—A solution of 0.50 g. (3.4 mmoles) of I in 1 ml. of acetic anhydride and 8 ml. of anhydrous benzene gave, after recrystallization from methanol (Norit), 0.54 g. (85%) of colorless plates: m.p. 224–226°; ν_{max}^{KBr} (cm.$^{-1}$) 3300 (s) (N–H), 1670 (s) (amide C=O), 1510 (m) (amide CONH); n.m.r. spectrum, benzene ring 7.1–7.8, CH (3-position) 6.90, CH_3 1.45.

Anal. Calcd. for $C_{10}H_9NOS$: C, 62.79; H, 4.74; S, 16.76. Found: C, 62.75; H, 4.95; S, 16.70.

Desulfurization of XI. β-Phenethylacetamide (XII).—A solution of 2.00 g. (0.01 mole) of XI in 400 ml. of absolute ethanol

(20) R. A. Smiley and C. Arnold, *J. Org. Chem.*, **25**, 257 (1960).

(21) Purified by drying over calcium hydride and distilling through a 30-cm., helices-packed column, b.p. 81–82° (13 mm.).

(22) E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry, and R. Winter *J. Am. Chem. Soc.*, **85**, 169 (1963).

(23) If the flask becomes too hot, the material will polymerize.

was heated under reflux overnight with freshly prepared Raney nickel (approximately 20 g.). The mixture was filtered, the filtrate was evaporated to dryness under reduced pressure, and the residue was distilled to yield 1.30 g. (80%): b.p. 110° (0.1 mm.); $\nu_{max}^{CHCl_3}$ (cm.$^{-1}$) 3290 (s) (NH), 1640 (s) (C=O). The infrared spectrum was identical with that of an authentic sample prepared by the method of Bischler and Napieralski.[24]

2-(N-Benzylidenamino)benzo[*b*]thiophene (XVIIa).—A solution of 220 mg. (2.0 mmoles) of benzaldehyde in 1 ml. of ethanol was added to a solution of 300 mg. (2.0 mmoles) of I in 3 ml. of ethanol; the resulting mixture was heated under reflux on a steam bath for 10 min. After the solution had cooled, the resulting product upon recrystallization from ethanol yielded 200 mg. (43%), m.p. 143–145°, $\nu_{max}^{10\%\ CHCl_3}$ (cm.$^{-1}$) 1620 (m) (C=N).

Anal. Calcd. for $C_{15}H_{11}NS$: C, 75.91; H, 4.67; S, 13.51. Found: C, 76.10; H, 4.75; S, 13.76.

2-(N-*p*-Chlorobenzylidenamino)benzo[*b*]thiophene (XVIIb).—A solution of 140 mg. (1.0 mmole) of *p*-chlorobenzaldehyde and 150 mg. (1.0 mmole) of I in 6 ml. of ethanol was heated under reflux for 1 min. on a steam bath to yield, after recrystallization from ethanol, 154 mg. (57%) of yellow needles, m.p. 194–195°, $\nu_{max}^{10\%\ CHCl_3}$ (cm.$^{-1}$) 1615 (m) (C=N).

Anal. Calcd. for $C_{15}H_{10}ClNS$: C, 66.29; H, 3.71; Cl, 13.05. Found: C, 66.18; H, 3.84; Cl, 13.07.

Diazotization of 2-Aminobenzo[*b*]thiophene (I). A. 2-Bromobenzo[*b*]thiophene (XIII).—To 1.50 g. (0.01 mole) of I in 12 ml. of 20% hydrobromic acid was added an aqueous solution of 0.70 g. (0.01 mole) of sodium nitrite at 0°. To the cooled solution was added a solution of 2.16 g. (0.015 mole) of cuprous bromide in 15 ml. of 20% hydrobromic acid. The mixture was allowed to come to room temperature slowly with stirring (2 hr.) and then was steam distilled. The distillate was saturated with sodium chloride and was extracted with three 20-ml. portions of ether. After the combined extracts were dried over magnesium sulfate, the ether was removed by distillation. Distillation of the residue yielded 0.95 g., b.p. 130–145° (17 mm.); the product solidified and was recrystallized from ethanol–water to yield 0.65 g. (31%) of 2-bromobenzo[*b*]thiophene (XIII), m.p. 38–39°. The infrared absorption spectrum was identical with that of an authentic sample prepared by treating 2-thianaphthenyllithium with bromine.[4]

B. 2-Keto-2,3-dihydrobenzo[*b*]thiophene (XVb).—A stirred suspension of 1.50 g. (0.01 mole) of I in a solution of 5 ml. of concentrated sulfuric acid and 10 ml. of water was cooled to below 5°, and a solution of 1.00 g. of sodium nitrite in 5 ml. of water was added. After this solution had been stirred for 5 min., it was added to a hot solution of 10 ml. of concentrated sulfuric acid and 10 ml. of water. This mixture was heated at 115° for 15 min. and then was steam distilled. The distillate was saturated with sodium chloride and was extracted with ether. The ether extracts were combined and dried over magnesium sulfate. After solvent removal, the residue was distilled to yield 0.50 g. (34%), b.p. 130–135° (14 mm.), m.p. 43–45°. The infrared absorption spectrum (neat film) was identical with that of a sample of "2-hydroxythianaphthene" (XVa) prepared by the method of van Zyl, *et al.*[15]

Actually, XVb could be formed by direct acidic hydrolysis. A solution of 2.00 g. (0.014 mole) of I in 100 ml. of 6 *N* hydrochloric acid and 40 ml. of tetrahydrofuran was heated under reflux for 3 days. The oil which formed was extracted with ether (three 40-ml. portions); the ether extracts were washed with saturated sodium chloride solution and dried over magnesium sulfate. After ether removal, the residue was distilled to yield 1.80 g. (90%) of product, b.p. 50–60° (0.05 mm.); crystallization of a sample from petroleum ether (b.p. 30–60°) gave a substance, m.p. 44–45°, identical with that produced by way of the diazotization procedure, as confirmed by the identity of the infrared absorption spectra: ν_{max} (cm.$^{-1}$) 1700 (w) (thiolactone C=O).

(24) A. Bischler and B. Napieralski, *Ber.*, **26**, 1903 (1893).

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Acenaphthene Chemistry. VIII.[1,2] The Oxidation of 5-Benzenesulfonamidoacenaphthene with Lead Tetraacetate. Two New Acenaphthene Compounds with Imidol Structures

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The oxidation of 5-benzenesulfonamidoacenaphthene with lead tetraacetate produced a mixture of substances. With the aid of methanol as an extraction solvent there was obtained 2-acetoxy-5-benzenesulfonimido-2a-acenaphthenequinol acetate (V), 2,3-diacetoxy-2a-methoxy-5-benzenesulfonimido-2a,5-dihydroacenaphthene (VI), 5-benzenesulfonamidoacenaphthylene (VII), and benzenesulfonamide.

Derivatives of acenaphthene in which the acenaphthene nucleus is a part of a quinoid structure have not been studied extensively. Rowe and Davies[3] reported what they believed to be the dioxime of 4,5-acenaphthenequinone, but this product, described as a brown, amorphous, infusible powder has not been adequately characterized. An acenaphthene compound with an *o*-imidol structure, 4,5-acenaphthenequinonedibenzenesulfonimide (I), has been described.[4]

An acenaphthene with a related structure was recently reported by Wittig, Reppe, and Eicher.[5] They described the structure II which was obtained by treating acenaphthylene with trityl sodium and trapping the intermediate with triphenylboron, followed by hydrolysis of this intermediate.

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(2) This work was supported by Public Health Service Research Grant CA 02997-6 from the National Cancer Institute, National Institutes of Health, and by a Shell Oil Co. Fellowship.

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