precipitate of silver bromide with alcoholic silver nitrate; infrared spectrum: 3.28, 3.33, 6.23, 6.71, 6.90, 6.98, 8.13, 8.23, 13.2 (broad), 13.6–13.9 (very broad), and 14.5 μ.

Anal. Calcd. for $C_{14}H_{13}Br$: C, 64.38; H, 4.98. Found: C, 64.76; H, 4.99.

o,o'-**Dibenzylbibenzyl** (II).—To 2.6 g. (10 mmoles) of V was added 0.3 g. (13 mg.-atoms) of sodium, freshly cut into small slices, and the mixture was heated at about 100° for 4 hr. under nitrogen. After the addition of 95% ethanol to consume unchanged sodium, water was added, and the solution was concentrated. Ether extraction gave a fluorescent oily product which partially crystallized on standing overnight. Addition of pentane and cooling in a Dry Ice–acetone bath caused further crystallization. The crude, oily solid, m.p. 92–93°, was recrystallized several times from pentane, eventually yielding 0.2 g. (11%) of II, m.p. 96–97°, as white crystals; infrared spectrum: 3.26, 3.32, 3.43, 6.22, 6.70, 6.88, 9.15, 9.29, 9.47, 12.65, 12.98, 13.44, 13.71, and 14.47 μ. This spectrum was identical in every respect with that of the product of the Raney nickel desulfurization of I.

Anal. Calcd. for $C_{28}H_{26}$: C, 92.77; H, 7.23. Found: C, 93.22; H, 7.17.

The oily residues appeared to consist primarily of II, which was probably contaminated by small amounts of isomeric hydrocarbons that could not be separated by repeated crystallizations or by elution chromatography. The infrared spectrum of this oil in chloroform was essentially identical with that of II in chloroform.

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Electrophilic Attack at the 2-Methyl Group of 2,3-Dimethylbenzo[*b*]thiophene

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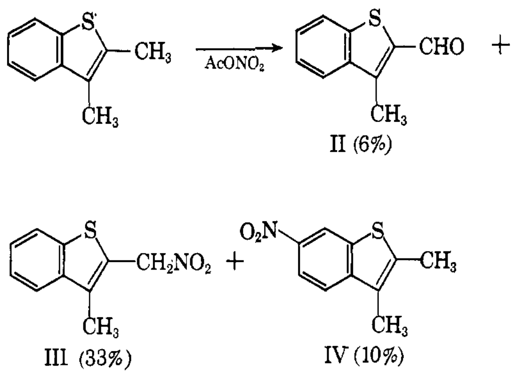
Benzo[*b*]thiophene undergoes electrophilic substitution preferentially in the 3-position, the 2-position being somewhat less active.[1] One of our objectives in studying the nitration of 2,3-dimethylbenzo[*b*]thiophene was to determine what position(s) in the benzene portion of the molecule would be attacked when the active 2- and 3-positions were blocked by methyl groups. Surprisingly enough, reaction occurred chiefly at the 2-methyl group, rather than on the aromatic nucleus. Thus, addition of 2,3-dimethylbenzo[*b*]thiophene to acetyl nitrate in acetic anhydride–acetic acid solution at 0° with a reaction time of 20 min. gave the results shown in eq. 1 (the remainder of the material appeared to be polymeric).

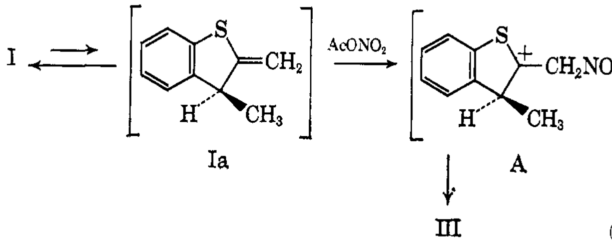
The yields of these three products were lowered on prolonged contact with the reaction mixture. Inverse addition gave 18% of II and very small amounts of nitro compounds.



(1)

The structure of II was established by reducing it to the known 3-methyl-2-hydroxymethylbenzo[*b*]thiophene. The structure of III followed from its conversion to the same alcohol by reduction and diazotization of the resulting amine. The structure of IV was assigned by virtue of the identity of its 1,1-dioxide with that obtaining by nitrating 2,3-dimethylbenzo[*b*]thiophene 1,1-dioxide. The latter will almost certainly substitute in the 6-position by analogy with the behavior of benzo[*b*]thiophene 1,1-dioxide.[2]

The unusual course of this nitration must be a consequence of the tendency of I to exist to some extent in a tautomeric form (Ia), which should be much more subject to electrophilic attack than is I.[3] Although formation of Ia requires loss of aromaticity in the thiophene ring, this is offset to some degree by the relief of strain between the two methyl groups and between the *peri* hydrogen (4-position) and the 3-methyl group. Formation of III from Ia by attack of NO_2^+, or the like, would be anticipated *via* intermediate A. Several mechanisms for the formation of II can be imagined, but there is no experimental evidence on this point yet.



(2)

To our knowledge this is the first report of the preferential attack of an electrophilic reagent at an alkyl group attached to an aromatic nucleus. It is to be expected, however, that other examples will be found in polyalkyl aromatics where tautomerism is favored by relief of alkyl–alkyl oppositions and/or a relatively low degree of aromaticity in the system.[4] Work in this area is continuing.

Experimental[5]

2,3-Dimethylbenzo[*b*]thiophene (I).—In a variation of Werner's method[6] a mixture of 47.5 g. (0.264 mole) of 3-phenylthio-2-butanone, 400 g. of polyphosphoric acid, and 20 g. of phosphorus pentoxide was heated to 120° for 4 hr. with occasional stirring.

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(1) See H. D. Hartough and S. L. Meisel, "Compounds with Condensed Thiophene Rings," Interscience Publishers, Inc., New York, N. Y., 1954, pp. 45–50, 116.

(2) F. Challenger and P. H. Clapham, *J. Chem. Soc.*, 1615 (1948).

(3) The n.m.r. spectrum of I in carbon tetrachloride shows two methyl absorptions of equal intensity at τ 7.67 and 7.87, and a multiplet at τ 2.38 to 2.97. Since there is no indication of the presence of Ia in the n.m.r. or infrared spectrum of I, the reactivity of Ia must be several powers of ten greater than that of I, but this is to be expected.

(4) Other examples of side-chain nitrations of alkyl benzenes have been recorded, but these are probably radical reactions (see A. V. Topchief, "Nitration of Hydrocarbons and Other Organic Compounds," Pergamon Press, Inc., New York, N. Y., 1959, pp. 157–160, 168–177.)

(5) Microanalyses were by Miss Hilda Beck. N.m.r. spectra were recorded at 60 Mc. by Larry Shadle.

(6) E. G. G. Werner, *Rec. trav. chim.*, **68**, 509 (1949).

After processing,[6] there was obtained 35.0 g. (82%) of colorless material, b.p. 96–98° (1.5 mm.), $n^{20}\text{D}$ 1.6165. Upon refrigeration crystals, m.p. 9°, were obtained.

Nitration of I.—A solution of 1.8 g. (0.011 mole) of I in 5 ml. of acetic anhydride was cooled to 5° and added rapidly with stirring to a nitrating solution, prepared at room temperature by adding (with cooling) 0.70 ml. (0.011 mole) of 70% nitric acid to 5 ml. of acetic anhydride and cooling to −5°. Despite ice–salt cooling, the temperature rose to 35° before slowly returning to 0°. After 20 min. the mixture was poured into ice–water. After hydrolysis, the solution was neutralized with sodium bicarbonate and extracted with ether. The 1.8 g. of yellow solid obtained on concentration of the ether layer was chromatographed on silica gel, eluting with hexane and finally ether–hexane. In this manner there was obtained, in order of elution, 0.22 g. (9.6%) of IV, m.p. 124–125°; 0.75 g. (32.6%) of III, m.p. 103–104°; 0.12 g. (6.1%) of II, m.p. 88–89°; and 0.45 g. of polymeric material. From a similar run, except that the nitration mixture was allowed to stand overnight at 0° prior to processing, the yields were much lower, larger amounts of polymeric material being formed. In this run a small amount of an additional product, m.p. 159–160°, crystallized from the hexane solution being prepared for chromatography. When the nitrating solution was added to a solution of I at 0° and the mixture was allowed to stand overnight at 0° and processed as before, the yields of IV and II were 2% and 18%, respectively; no III was isolated, the major amount of material was polymeric.

3-Methyl-2-benzo[*b*]thiophenecarboxaldehyde (**II**) was obtained as pale yellow needles, m.p. 88–89°. In addition to a strong $C{=}O$ band at 6.02 μ, it had an aldehydic C–H band at 3.50 μ, and other infrared peaks at 3.25, 3.42, 6.23, 6.36, 6.52, 6.96, 7.23, 7.40, 7.55, 7.87, 8.20, 8.58, 9.25, 9.40, 10.64, 13.19, 13.72, 13.92, 14.83, and 15.15 μ. The n.m.r. spectrum in carbon tetrachloride showed a singlet at τ −0.23 for the aldehydic proton, a multiplet from τ 2.12 to 2.67 for the aromatic protons, and a singlet at τ 7.32 for the methyl group.

Anal. Calcd. for $C_{10}H_8OS$: 68.18; H, 4.58. Found: 68.02; H, 4.49.

The **oxime**, recrystallized from hexane, melted at 161–162°.

Anal. Calcd. for $C_{10}H_9NOS$: C, 62.82; H, 4.75; N, 7.33. Found: C, 62.66; H, 5.01; N, 7.29.

3-Methyl-2-nitromethylbenzo[*b*]thiophene (**III**) was obtained as nearly colorless crystals, m.p. 103–104°. It dissolved slowly in warm dilute sodium hydroxide and was recovered by acidification. The infrared spectrum showed strong unconjugated nitro peaks at 6.45 and 7.30 μ, and other peaks at 3.35, 3.51, 6.99, 7.45, 7.66, 8.24, 8.52, 8.63, 8.80, 9.41, 9.82, 10.82, 12.47, 12.70, 13.19, 13.70, 14.00, and 14.89 μ. The n.m.r. spectrum showed a multiplet from τ 2.18 to 2.77 for the aromatic protons, a singlet at τ 4.48 for the methylene α to the nitro, and a singlet at τ 7.60 for the methyl group.

Anal. Calcd. for $C_{10}H_9NO_2S_2$: C, 57.97; H, 4.38; N, 6.76. Found: C, 57.85; H, 4.56; N, 6.32.

2,3-Dimethyl-6-nitrobenzo[*b*]thiophene (**IV**) was obtained as bright yellow needles, m.p. 124–125°. The infrared spectrum showed strong conjugated nitro peaks at 6.60 and 7.48 μ, and other peaks at 3.20, 3.40, 6.22, 6.42, 6.82, 7.10, 7.16, 8.46, 8.77, 8.89, 9.56, 1.12, 11.25, 11.92, 12.18, 12.59, 13.27, and 13.88 μ. The n.m.r. spectrum (τ) in carbon tetrachloride showed the aromatic protons individually as follows: a doublet at τ 1.67 (J = 2 c.p.s.) for the 7-*H;* a pair of doublets at 2.10 (J_1 = 9 c.p.s., J_2 = 2 c.p.s.) for the 5-*H;* and a doublet at 2.67 (J = 9 c.p.s.) for the 4-*H*. The methyl groups gave two singlets of equal intensity at 7.53 and 7.77.

Anal. Calcd. for $C_{10}H_9NO_2S$: C, 57.97; H, 4.38; N, 6.76. Found: C, 58.39; H, 4.53; N, 6.47.

3-Methyl-2-hydroxymethylbenzo[*b*]thiophene (**V**).—A solution consisting of 10 ml. of 95% alcohol, 0.40 g. (0.0025 mole) of II, and 0.05 g. (0.0013 mole) of sodium borohydride was allowed to stand for 1 hr. A pellet of sodium hydroxide was added, and the alcohol was removed by distillation, adding water to maintain the volume. The crude alcohol, which separated on cooling, was recrystallized from ether–hexane to give 0.22 g. (54%) of material, m.p. 90–91°, lit.[7] m.p. 90.6–91.6°. Infrared peaks were at 3.05, 3.40, 3.48, 6.82, 6.95, 7.22, 7.33, 8.47, 8.60, 8.77, 10.0 broad, 10.65, 13.20, 13.67, 14.00, and 14.55 μ. The n.m.r. spectrum in carbon tetrachloride showed a multiplet from τ 2.38 to 2.98 for the aromatic protons, a singlet at 5.40 for the methylene group, a singlet at 6.83 for the hydroxylic proton, and a singlet at 7.83 for the methyl group.

3-Methyl-2-aminomethylbenzo[*b*]thiophene Hydrochloride.—A solution of 0.1 g. of lithium aluminum hydride and 0.20 g. (0.0010 mole) of III in 25 ml. of ether was refluxed overnight, and water was added dropwise to decompose the excess reducing agent. Excess dilute sodium hydroxide was added to dissolve the aluminum hydroxide, and the solution was extracted with ether. The amine was extracted from the ethereal solution with dilute hydrochloric acid, the acid extract was neutralized, and the amine, 0.1 g. (56%), m.p. 59–60°, was recovered by ether extraction. On drying *in vacuo,* it was converted to a brown oil. The latter was treated with dilute hydrochloric acid to give a sparingly soluble hydrochloride, which was collected on a filter and washed with ether and with water; the solid melted at 220° with decomposition.

Anal. Calcd. for $C_{10}H_{11}NS{\cdot}HCl$: N, 6.56. Found: N, 6.43.

An excess of cold aqueous sodium nitrite was added to a cold solution of the amine hydrochloride dissolved in dilute hydrochloric acid. After standing at room temperature for an hour, the solution was warmed briefly on the steam bath, cooled, and extracted with ether. After crystallization from pentane, V, m.p. 91–92°, was recovered from the ether solution (identity was established by its infrared spectrum and a mixture melting point determination).

2,3-Dimethyl-6-nitrobenzo[*b*]thiophene 1,1-Dioxide.—Oxidation of 1.0 g. of I with 2.5 ml. of 40% peracetic acid in 10 ml. of acetic acid gave 0.95 g. (79%) of the 1,1-dioxide, m.p. 150–151°, lit.[6] m.p. 149–150°. The n.m.r. spectrum in 1,1,2,2-tetrachloroethane showed a multiplet at τ 2.38 to 2.60 and a singlet at 7.87 for the two methyl groups. A 0.85-g. sample of the dioxide was dissolved in 5 ml. of concentrated sulfuric acid, the solution was cooled to 0°, and a solution of 0.27 ml. of concentrated nitric acid in 1 ml. of concentrated sulfuric acid was added dropwise. Processing in the usual manner gave a product, m.p. 199–200° after two crystallizations from 95% alcohol. This material had an infrared spectrum identical with that of a sample of 2,3-dimethyl-6-nitrobenzo[*b*]thiophene 1,1-dioxide, m.p. 201–202°, obtained in 71% yield by oxidation of IV with 40% peracetic acid, and a mixture melting point determination showed no depression. The n.m.r. spectrum in 1,1,2,2-tetrachloroethane showed a singlet (1.5) at τ 1.48 and a doublet (0.5) at τ 1.64 (J = 2. c.p.s.), which probably resulted from superimposition of a doublet at τ 1.48 (J = 2 c.p.s.) for the 7-*H* aromatic proton with a pair of doublets centered at 1.57 (J_1 = 9 c.p.s., J_2 = 2 c.p.s.) for the 5-*H* aromatic proton. There was a doublet (1) at τ 2.47 (J = 9 c.p.s.) for the 4-*H* aromatic proton and a singlet (6) at 7.80 for the two methyl groups.

Anal. Calcd. for $C_{10}H_9NO_4S$: C, 50.21; H, 3.79; N, 5.86. Found: C, 50.64; H, 3.72; N, 5.94.

Acknowledgment.—This work was supported by the American Petroleum Institute under Project 48B.

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[7] R. Gaertner, *J. Am. Chem. Soc.*, **74**, 2185 (1952). The isomer, 2-methyl-3-hydroxymethylbenzo[*b*]thiophene, is reported to melt at 145.8–147.4° [**74**, 766 (1952)].

Preparation of 5-Dinitromethyltetrazole from Salts of Dinitroacetonitrile

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A general method for preparing tetrazoles by the reaction of nitriles with sodium azide in the presence or absence of ammonium ion in dimethylformamide has recently been described.[1,2] We attempted to extend

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[1] W. G. Finnegan, R. A. Henry, and R. Lofquist, *J. Am. Chem. Soc.*, **80**, 3908 (1958).

[2] W. P. Norris, *J. Org. Chem.*, **27**, 3248 (1962).