tected nucleoside **7** which was then treated with chloroform, leaving 1.0 g. of insoluble material. After evaporation of the solvent, the chloroform-soluble material was placed on a column (3 × 26 cm.) of 80 g. of silicic acid (Fisher reagent grade, activated for 1 hr. at 105°) and was eluted with chloroform–methanol (95:5), 2.5-ml. eluates being collected. The desired material, amounting to 240 mg., appeared in fractions 141–200, and was then dissolved in 40 ml. of absolute ethanol saturated with ammonia at 0°. After stirring in a closed flask for 24 hr., the insoluble material was filtered and the filtrate was evaporated to dryness. The residue was dissolved in 10 ml. of methanol, 100 mg. of picric acid was added, and, after standing for 5 hr., the resulting yellow salt was collected. It was next treated in water for 18 hr. with 10 ml. of Amberlite IR-45 ion-exchange resin and, after filtering, the clear solution was evaporated to dryness at 30°. Recrystallization of the residue from 95% ethanol gave 80 mg. (8.4% based on **1**) of pure 9-(2-deoxy-D-*ribo*-hexopyranosyl)-adenine (**8**) as a hemihydrate, m.p. 159–164°, $[\alpha]^{23}$D +74.9° (*c* 0.833, methanol), $\lambda_{max}^{H_2O}$ 259.5 mμ (log ε 4.22). When chromatographed on paper the nucleoside **8** traveled as a single spot ($R_{adenine}$ 1.11). On t.l.c. chromatograms the R_f value was 0.75.

Anal. Calcd. for $C_{11}H_{15}N_5O_4 \cdot 0.5\ H_2O$: C, 45.51; H, 5.55; N, 24.12. Found: C, 45.43; H, 5.97; N, 24.29.

Anomeric (?) Nucleoside 8.—The chloroform-insoluble fraction of the protected nucleoside **7** obtained in the preceding experiment was placed on a column (3 × 26 cm.) of 60 g. of silicic acid (activated for 1 hr. at 105°) and 40 g. of Celite 505, similarly dried. Elution, in 2.5-ml. fractions, was carried out using ethyl acetate, and from fractions 21–36 there was obtained 500 mg. of material which was deacylated and treated in the same manner as that described in the foregoing experiment. The white powder obtained was recrystallized from 95% ethanol giving 30 mg. (3.2% based on **1**) of hydrated nucleoside, m.p. 143–150°, $[\alpha]^{23}$D +49.5° (*c* 0.370, methanol), $\lambda_{max}^{H_2O}$ 260 mμ (log ε 4.10). When chromatographed on paper, the material traveled as a single spot ($R_{adenine}$ 1.11). On t.l.c. chromatograms the R_f value was 0.75.

Anal. Calcd. for $C_{11}H_{15}N_5O_4 \cdot H_2O$: C, 44.14; H, 6.72; N, 23.40. Found: C, 44.87; H, 6.00; N, 23.54.

Acknowledgment.—For the elemental analyses the authors are indebted to Miss Paula Parisius, Microanalytical Laboratory, LC, NIAMD, National Institutes of Health, Bethesda, Maryland, under the direction of Mr. H. G. McCann.

3,3′-Diphenyl-1,1′-bibenzo[*c*]thienyl

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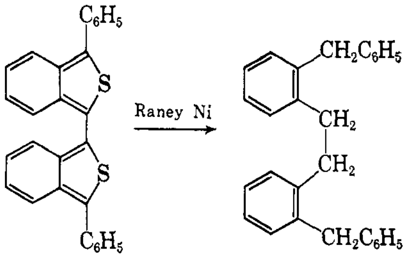
Received September 12, 1963

In a survey of known derivatives of benzo[*c*]thiophene[1] our attention was directed to a red compound, m.p. 237°, obtained by heating *o*-benzoylbenzoic acid with phosphorus pentasulfide,[2] which was reported to be 1-phenylbenzo[*c*]thiophene. Since 1,3-diphenylbenzo[*c*]thiophene, for which the structure is firmly established,[3] is yellow and melts at 118–119°, the color and melting point of the supposed 1-phenylbenzo[*c*]thiophene seemed out of line. Investigation has shown this compound to be 3,3′-diphenyl-1,1′-bibenzo[*c*]thienyl (I).



I II

Structure proof was accomplished by desulfurization of I to *o*,*o*′-dibenzylbibenzyl (II).

This structure assignment was supported by examination of the mass spectrum, which had a parent peak at 418 (98%) and a peak at mass 354 ascribable to the loss of two sulfur atoms. This shows that the original molecular weight determination (223 and 239 found[2]) must have been in error.

Experimental[4]

3,3′-Diphenyl-1,1′-bibenzo[*c*]thienyl (I).—This compound was prepared as described by O'Brochta and Lowy[2] (termed 2-phenyl-3,4-benzothiophene). Deep red needle-like crystals of I, m.p. 236–237°, were obtained in 15% yield; infrared spectrum: 3.28, 6.26, 6.69, 6.92, 7.34, 7.57, 8.29, 9.23, 9.68, 10.80, 11.70, 11.89, 13.1 (broad), 13.4 (very broad), and 14.4 (very broad) μ; mass spectrum: parent peak at 418 (98%) and peak at 354, due to loss of both sulfur atoms. No peaks attributable to (isotopic) oxygen.

Anal. Calcd. for $C_{28}H_{18}S_2$: C, 80.37; H, 4.33; S, 15.30. Found: C, 79.67; H, 4.31; S, 15.50. Reported in ref. 2: C, 80.01, 80.29; H, 4.72, 4.73; S, 15.02.

Desulfurization of I with Raney Nickel.—A mixture of 1.7 g. (4.1 mmoles) of I, approximately 20 g. of Raney nickel, and 50 ml. of 95% ethanol was refluxed for 2 days. The insoluble residue was removed by filtration, and the filtrate was concentrated until solid material crystallized. Recrystallization from 95% ethanol afforded 1.0 g. (68%) of a white crystalline compound, m.p. 97–98°, identified as *o*,*o*′-dibenzylbibenzyl (II) by comparison with an authentic sample, synthesized as described below. The infrared spectra were identical in all respects, and the mixture melting point was undepressed.

***o*-Benzylbenzyl Alcohol (IV).**—This compound was prepared from *o*-benzylbenzoic acid[5] as described by Speeter.[6] IV was obtained as a colorless liquid, b.p. 147–148° (1 mm.), n^{20}D 1.5942, lit.[6] b.p. 148–151° (3 mm.). Upon standing at room temperature, the alcohol solidified. Recrystallization from hexane gave white needle-like crystals of IV, m.p. 37–38°; infrared spectrum: broad O–H at 3.0, 6.22, 6.70, 6.89, 9.6–10.0 (broad bands), 13.2–13.7 (broad bands), and 14.5 μ.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 85.26; H, 7.18.

The **phenylurethan derivative** melted at 60–61°, lit.[6] m.p. 77–78°; infrared spectrum: 3.08 (N–H), 5.92 (C=O), 6.25, 6.56, 6.94, 7.62, 8.05, 8.16, 9.43, 13.16, 13.85, and 14.50 μ.

Anal. Calcd. for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41. Found: C, 80.16; H, 6.33; N, 4.56.

***o*-Benzylbenzyl Bromide** (V).—To a solution of 12.8 g. (64.6 mmoles) of IV in 20 ml. of benzene, cooled in an ice bath, was added dropwise 6.0 g. (22 mmoles) of phosphorus tribromide over a 15-min. period. The mixture was stirred overnight while coming to room temperature and allowed to stand until a total reaction time of 24 hr. had elapsed. Work-up in the usual manner afforded 17.0 g. of a crude oily product which crystallized when placed in a Dry Ice–acetone bath. Recrystallization from hexane gave 13.0 g. (77.1%) of white needle-like crystals of V, m.p. 40–42°. Further recrystallization from hexane gave the analytical sample, m.p. 42–43°. V gave an immediate

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[1] The parent compound has been synthesized recently by R. Mayer, *et al.*, *Angew. Chem.*, **74**, 118 (1962); *Angew. Chem., Intern. Ed. Eng.*, **1**, 115 (1962).

[2] J. O'Brochta and A. Lowy, *J. Am. Chem. Soc.*, **61**, 2765 (1939).

[3] See H. D. Hartough and S. L. Meisel, "Compounds with Condensed Thiophene Rings," Interscience Publishers, Inc., New York, N. Y., 1954, pp. 169–170.

[4] Carbon, hydrogen, and nitrogen analyses were by Miss Hilda Beck. Sulfur analysis was by Micro-Tech Laboratories, Skokie, Ill. All infrared spectra were taken in potassium bromide pellets.

[5] E. L. Martin, *J. Am. Chem. Soc.*, **58**, 1441 (1936).

[6] M. E. Speeter, U. S. Patent 2,759,934; *Chem. Abstr.*, **51**, 2044 (1957).

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.

Acknowledgment.—This work was supported by the American Petroleum Institute under Project 48B. We wish to thank Dr. G. P. Hinds of the Shell Oil Company, Deer Park, Texas, for the determination of the mass spectrum.

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

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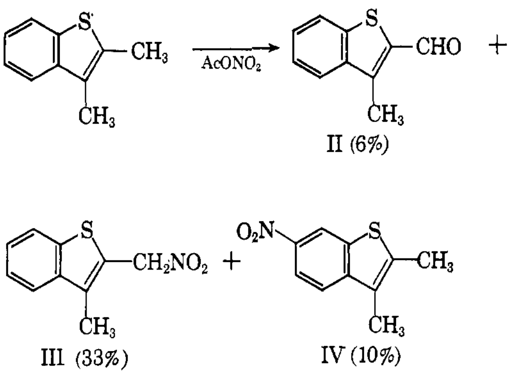
Benzo[*b*]thiophene undergoes electrophilic substitution preferentially in the 3-position, the 2-position being somewhat less active.[1] One of our objectives in studying the nitration of 2,3-dimethylbenzo[*b*]thiophene was to determine what position(s) in the benzene portion of the molecule would be 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).

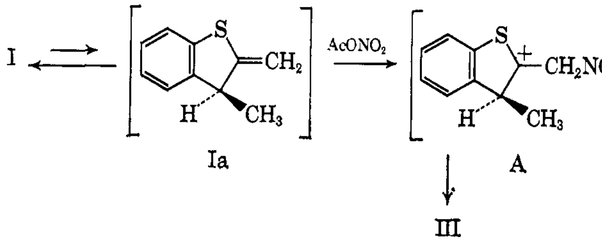


(1)

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.

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).