Preparation and Ultraviolet Absorption Spectra of the Isomeric Naphthobenzothiophenes and Naphthobenzofurans. (1)

E. Campaigne and S. W. Osborn (2)

Department of Chemistry, Indiana University

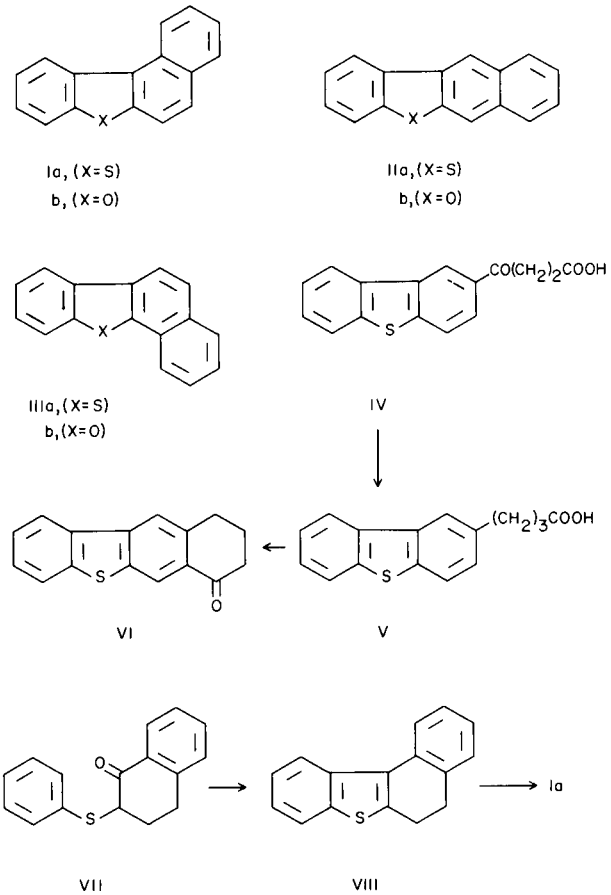
Naphtho[2,1-*b*]benzothiophene has been synthesized unequivocally by the ring closure of 2-phenylmercapto-1-tetralone, followed by dehydrogenation of the resulting dihydro derivative. The other isomeric naphthobenzothiophenes have been prepared by modifications of known methods and their ultraviolet absorption spectra have been compared.

Condensation of α-naphthol with 2-chlorocyclohexanone leads to 7,8,9,10-tetrahydronaphtho-[1,2-*b*]benzofuran, which can be readily dehydrogenated with selenium to naphtho[1,2-*b*]-benzofuran. The ultraviolet spectra of the naphthobenzofurans are reported, and compared to their sulfur analogs.

Certain of the alkyl derivatives of the naphthobenzothiophenes are of interest in connection with the study of various sulfur analogs in the 1,2-benzanthracene series. Their preparation, however, involves methods which leave some doubt as to the final ring structure. These same problems appear in the naphthobenzofuran series. For this reason, the six basic ring structures (I-III) have been synthesized and their properties, including the ultraviolet absorption spectra, have been compared as a possible means of structure proof.

The synthesis of naphtho[2,1-*b*]benzothiophene (Ia) has been reported by Bordwell, McKellin, and Babcock (3) who found that benzothiophene 1,1-dioxide dimerized on heating, with loss of sulfur dioxide, to give a new dioxide. This substance, after aromatization and reduction of the dioxide, yielded a compound to which they assigned structure Ia.

Compound IIa has been prepared by the reduction of 6,11-benzo[*b*]thiophanthraquinone with zinc dust (4), and by heating 2-phenylnaphthalene with sulfur in the presence of aluminum chloride (5). For the preparation of alkyl derivatives, however, the best method, suggested by Gilman and Jacoby (6), involves the succinoylation of dibenzothiophene with succinic anhydride, followed by reduction of the ketone (IV) and cyclodehydration of the resulting γ-2-dibenzothienylbutyric acid (V). Gilman and Jacoby predicted that cyclization would occur in the 3-position of dibenzothiophene rather than the 1-position. This has been confirmed by Buu-Hoi and Cagniant (7) and by Werner (8) who reduced and dehydrogenated ketone VI to get IIa.



An attractive synthesis of dibenzothiophene itself has been reported by Rabindran and Tilak (9) which has

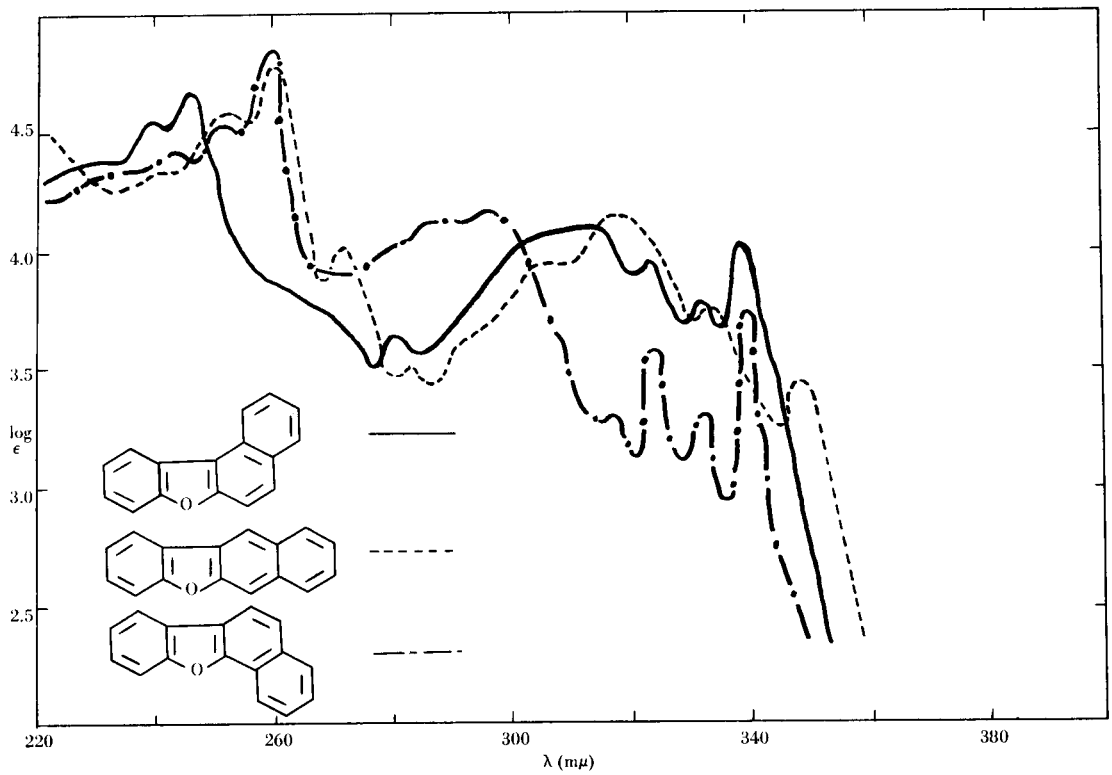


Figure 1. Ultraviolet Absorption Spectra of Isomeric Naphthobenzofurans

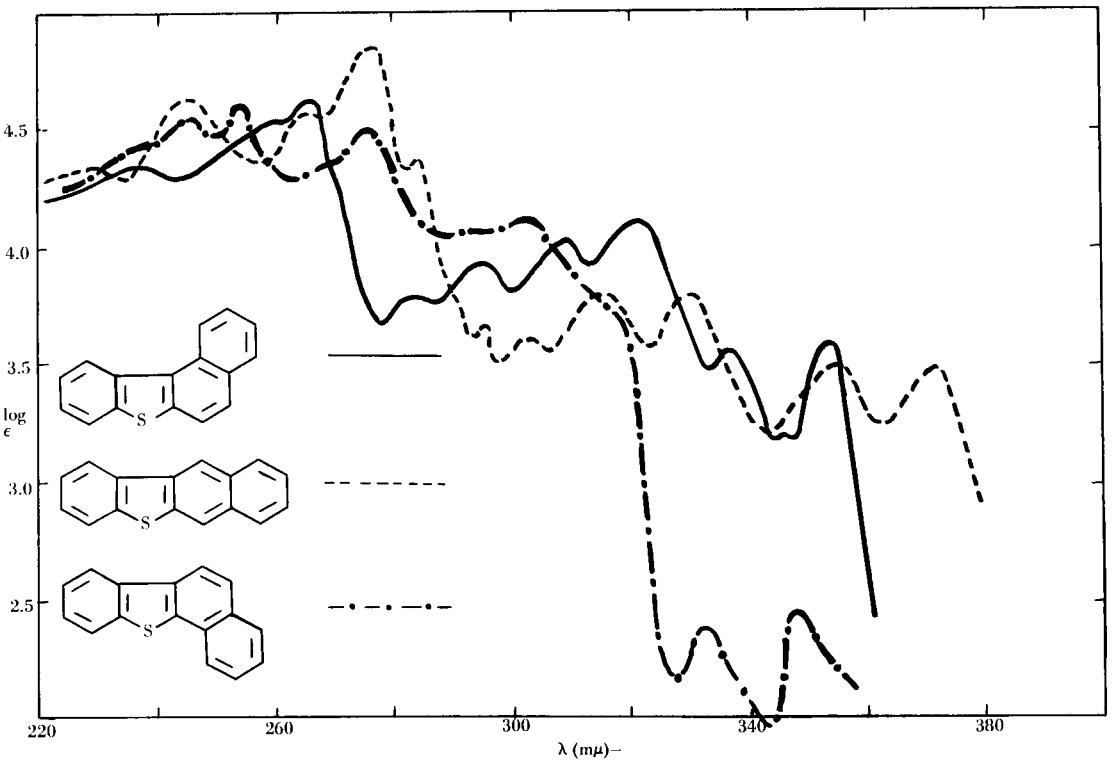


Figure 2. Ultraviolet Absorption Spectra of Isomeric Naphthobenzothiophenes

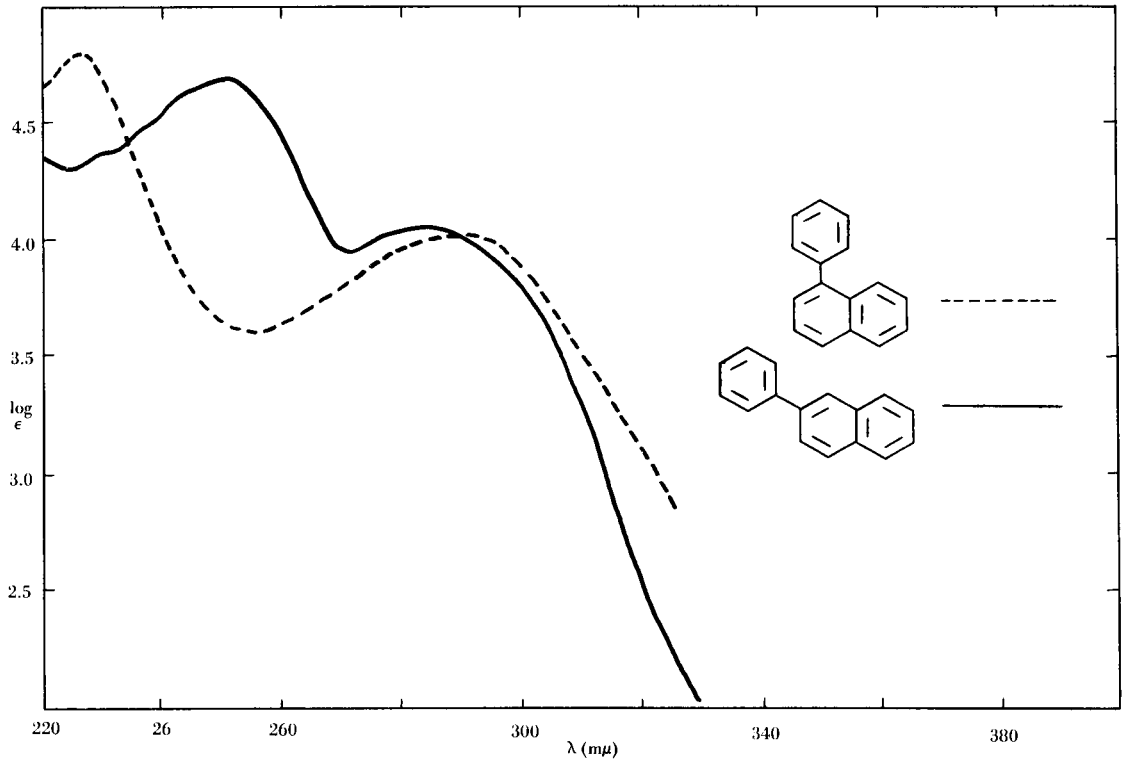


Figure 3. Ultraviolet Absorption Spectra of Phenylnaphthalenes, from Friedel, "Ultraviolet Spectra of Aromatic Compounds," New York, John Wiley and Sons, 1951.

been extended to include compounds Ia and IIIa (10). Thiophenol was condensed with 2-bromocyclohexanone in the presence of sodium ethoxide (11) to yield a ketosulfide which underwent cyclodehydration in the presence of phosphoric anhydride to yield tetrahydrodibenzothiophene (12). Dehydrogenation with selenium gave excellent yields of dibenzothiophene. Through the substitution of 1- and 2-thionaphthols for thiophenol, the synthesis of Ia and IIIa was likewise accomplished. The structure of compound IIIa was established through the condensation of 2-bromocyclohexanone with 8-chloro-1-thionaphthol. Cyclization of this sulfide can occur only in the 2-position of the naphthalene nucleus, and dehydrogenation and dechlorination thus yielded IIIa unequivocally. The structure of Ia was established by its nonidentity with IIa and IIIa.

In the present work, compound Ia has been prepared through the condensation of thiophenol with 2-bromo-1-tetralone, to form the keto-sulfide (VII), followed by ring closure to the dihydro derivative (VIII). Cyclization can occur here in only one way, yielding compound Ia unequivocally on dehydrogenation. Furthermore, a mixed melting point showed that this compound and that of Bordwell, McKellin and Babcock (13) are identical, giving additional confirmation to the structure.

During the preparation of compound IIa by the method of Gilman and Jacoby, it was found advantageous to use the Huang-Minlon modification of the Wolff-Kischner reduction (14) for reduction of the ketones rather than the Clemmensen reduction. Not only were the yields improved, but the products were somewhat easier to purify. Upon recrystallization of V from aqueous methanol following Clemmensen reduction, small quantities of the methyl ester of V were always isolated.

Robinson and Mosettig (15) reported that in the cyclization of γ-2-dibenzofuranylbutyric acid, the oxygen analog of V, two ketones were isolated corresponding to the two possible directions of ring closure. The reagent used was a mixture of phosphoric acid and phosphoric anhydride. Although several different reagents were used to effect the reaction, including polyphosphoric acid, only compound VI was obtained by cyclization of V, as had been reported (6).

While powdered selenium was effective in the dehydrogenation of 1,2,3,4-tetrahydrodibenzothiophene, this reagent gave poor results in the naphthobenzothiophene series. Temperatures of 320 to 350° were required and the yields were low. In particular, VIII was difficult to

dehydrogenate with selenium and only traces of the product were obtained. In accord with findings of Rabindran and Tilak (16), a palladium-on-charcoal catalyst in refluxing xylene was found to be most effective in this series. These catalysts are easily poisoned, however, and it was necessary to conduct the reaction in a sulfur-free room and to use two or more portions of catalyst during the reaction, removing one by filtration before adding the next. Ring-bound sulfur, as in the benzothiophenes, does not appear to poison the catalyst, while thiols are active catalyst poisons.

The naphthobenzothiophenes, as well as their corresponding tetrahydro derivatives, were conveniently characterized by conversion to their sulfones, according to the method of Bordwell, Lampert, and McKellin (17).

For comparative purposes, it was desirable to obtain the ultraviolet spectra of the isomeric naphthobenzofurans Ib, IIb and IIIb. Naphtho[2,3-*b*]benzofuran (Brazan, IIb) (18) had been reported (15). The synthesis of naphtho[2,1-*b*]benzofuran (Ib) has recently been reported (19). Following this method, but without isolation of the intermediates, and using a selenium dehydrogenation, Ib, melting higher than previously reported, was obtained in 25% yield, based on β-naphthol.

Naphtho[1,2-*b*]benzofuran (IIIb) has been synthesized from 2-phenyl-3-carboxymethylbenzofuran by Chatterjea (20). Condensation of α-naphthol and 2-chlorocyclohexanone in the presence of potassium carbonate under nitrogen produced an oily mixture which, upon distillation produced the desired 7,8,9,10-tetrahydronaphtho[1,2-*b*]benzofuran. Aromatization of this compound produced IIIb, melting at 102-102.5°, as reported (20).

Discussion of Ultraviolet Absorption Spectra (21).

The ultraviolet absorption curves for compounds Ib, IIb and IIIb are reproduced in Figure 1. Three main regions of absorption are apparent, intense absorption at 240-260 mμ, a slightly weaker absorption between 300 and 320 mμ, and a third still less intense region from 320 to 350 mμ (22). The three isomers may be distinguished from one another by the principal absorption peaks in these three regions. Compound Ib is clearly identified by a strong peak at 247 mμ, in contrast to the peak at 260 mμ shown by the other two. On the other hand, IIIb is distinguished from Ib and IIb by the broad band of absorption at approximately 295 mμ, which is found in the range of 310-320 mμ in the other two. Finally, IIb differs from Ib and IIIb in that the latter two show a sharp peak at 340 mμ, while IIb absorbs less strongly at 355 mμ. The characterization of these three isomers is very clean cut, since each of the three regions of absorption serve to differentiate one of the isomers from the other two.

The spectra of the corresponding sulfur analogs, Ia, IIa and IIIa are shown in Figure 2. The same three regions of absorption, bathochromically shifted about 20 mμ, are obvious, and the three isomers may be distinguished in the same way.

The U. V. spectra of these various tetracyclic mid-ring heterocycles are characteristic of α- and β-substituted phenylnaphthalenes (compare Figure 3). Orchin and Friedel (23) compared the spectra of the isomeric benzofluorenes, I, II and III, (X = CH_2) and found these to correlate with the phenylnaphthalenes, particularly in the range of 240-270 mμ. Thus I (X = -CH_2-) shows a strong band at 230 mμ, and is a derivative of α-phenylnaphthalene, while II and III (X = -CH_2-) had identical strong bands at 265 mμ, and both of these are β-phenylnaphthalene derivatives. Clemo and Felton (24) have analyzed the ultraviolet spectra of the benzocarbazoles (I, II and III, X = NH) and found that these heterocycles also absorb as substituted naphthalenes, but that the bathochromic shifts are related to the nitrogen atom in the β-position, rather than phenyl, as in the case of the benzofluorenes. Apparently, then, all analogs of structures I, II and III may be considered as phenylnaphthalenes in general absorption characteristics in the range 230-290 mμ, but those with the strongest π-electron contributors in the β-positions will exhibit the greatest bathochromic shifts of λ max in this region. Thus, in Figure 1, oxygen is a weak π-electron contributor, even weaker than -CH_2-. Compound Ib with the strong π-electron contributor phenyl in the α-position absorbs at lower wave length than IIb and IIIb, both of which are β-phenylnaphthalenes having nearly identical absorption in range 240-260 mμ. Exactly the same analysis fits the sulfur analogs (Figure 2), except that sulfur is a better π-electron contributor than either oxygen or methylene, and hence the absorption maxima are shifted bathochromically. However, phenyl still dominates in this series, and Ia, and α-phenylnaphthalene analog, has a λ max at 265 mμ, while IIa and IIIa, β-phenylnaphthalene analogs, show the principal peak at 275 mμ.

In all cases, compounds of type II exhibit the absorption maxima at the longest wave lengths since they are naphthalenes substituted at both β-positions by electron releasing groups. Even 1,2-benzanthracene (II, X = -CH=CH-) fits this analysis, its principal λ max appearing at 286 mμ (25).

EXPERIMENTAL (26)

2-Phenylmercapto-1-tetralone (VII).

The general method of Rabindran and Tilak (9) was used. Metallic sodium (0.14 gram-atom) was dissolved in 150 ml. of absolute ethanol, and after solution, 15.4 g. (0.14 mole) of benzenethiol was added. The mixture was heated to reflux with

rapid stirring and 30 g. (0.135 mole) of 2-bromo-1-tetralone, prepared by the method of Wilds and Johnson (27), was added dropwise during 30 minutes. Reflux was continued, with stirring, for 4 hours. The mixture was cooled and acidified to litmus with alcoholic hydrogen chloride, and the sodium bromide was removed by filtration. The ethanol was evaporated under reduced pressure and the residue was vacuum-distilled from a Claisen head flask with short fractionating sidearm. About 5 g. of unreacted bromotetralone were recovered unchanged. The main fraction, boiling at 178°/0.5 mm, weighed 23.3 g., 69% based on the original quantity of bromoketone.

Anal. Calcd. for $C_{16}H_{14}OS$: C, 75.5; H, 5.5 S, 12.6. Found: C, 75.4; H, 5.6; S, 12.6.

A picrate was prepared by mixing alcoholic solutions of the compound and of picric acid, and allowing the mixture to stand in the refrigerator. Recrystallization from ethanol gave orange needles, melting at 106-106.5°.

Anal. Calcd. for $C_{22}H_{17}O_8N_3S$: C, 54.66; H, 3.55. Found: C, 54.70; H, 3.30.

A 2,4-dinitrophenylhydrazone was prepared by the method of Johnson (28) and recrystallized from ethanol, m.p. 202-203°.

Anal. Calcd. for $C_{22}H_{18}N_4O_4S$: C, 60.82; H, 4.18. Found: C, 60.41; H, 4.21.

5,6-Dihydroaphtho[2,1-*b*]benzothiophene (VIII).

Ten g. of VII was heated to 190-200° in an oil bath, and about 6 g. of phosphorus pentoxide was stirred slowly into the mixture. Two more 3 g. portions of phosphorus pentoxide were added at 15 minutes intervals and the gummy mass was stirred continuously with a glass rod. After 45 minutes the mixture was poured over ice and allowed to stand for several hours. The oil was removed and the aqueous layer extracted with ether. Oil and extracts were combined, washed with water, 5% sodium bicarbonate, and again with water. After drying and removal of the ether, the product was vacuum-distilled, b.p. 158-162°/0.5 mm., and 5.6 g., (60%) collected as a pale yellow viscous oil which could not be crystallized.

A picrate was prepared and recrystallized from ethanol, m.p. 147-148°.

Anal. Calcd. for $C_{22}H_{15}N_3O_7S$: C, 56.8; H, 3.2. Found: C, 57.0; H, 2.8.

A sulfone was prepared by oxidation with 30% hydrogen peroxide in acetic acid (1) to give 57% of a white crystalline product, melting at 119.5-120°.

Anal. Calcd. for $C_{16}H_{12}O_2S$: C, 71.61; H, 4.51; S, 11.95. Found: C, 71.30; H, 4.48; S, 11.89.

Naphtho[2,1-*b*]benzothiophene (Ia).

A solution of 2 g. of VIII in 50 ml. of xylene was shaken for 5 minutes with 0.3 g. of a 5% palladium-on-charcoal catalyst (American Platinum Works). The solution was filtered, transferred to a clean flask and refluxed for 5 hours with 0.5 g. of fresh catalyst. This catalyst was again removed by filtration and refluxing was continued with 0.4 g. of fresh 30% catalyst and another 0.2 g. of 30% catalyst was added after 4 hours. After a total of 13 hours the catalyst was removed by filtration and the xylene was evaporated in a stream of air. The residue was recrystallized from ethanol to yield 1.2 g. (60%) of white crystals melting at 101.5-102°, and a mixed melting point with a sample of Ia (13) melted at 101.5°.

Anal. Calcd. for $C_{16}H_{10}S$: C, 82.01; H, 4.30; S, 13.68. Found: C, 81.60; H, 4.48; S, 13.30.

The sulfone of Ia melted at 228-229° and the melting point was undepressed on mixing with an authentic sample (13).

γ-2-Dibenzothienylbutyric Acid (V).

The Huang-Minlon modification of the Wolff-Kishner reduction was used (14). Ten g. of β-2-dibenzothenoylpropionic acid (IV), prepared by the method of Gilman and Jacoby (6), 5 g. of sodium hydroxide, 80 ml. of diethylene glycol, and 5 ml. of 85% hydrazine hydrate were refluxed for 1 hour. Water was then allowed to distill slowly from the reaction mixture until the temperature of the boiling solution reached 195-200°. The mixture was boiled for 3 hours then cooled by the addition of ice. Dilute hydrochloric acid was added slowly with stirring until the solution was acid to litmus, and the precipitated product was collected, washed with water, and recrystallized from 80% methanol. The yields in several experiments were 82-90%. m.p. after one recrystallization, 130-131° (6).

4-Keto-1,2,3,4-tetrahydronaphtho[2,3-*b*]benzothiophene (VI).

Ring closure of V by the method of Gilman and Jacoby (6) yielded 35-50% of product. Substitution of polyphosphoric acid for sulfuric acid in the above reaction yielded only 11-35% of VI. The most satisfactory cyclization procedure was a modification of that of Bachmann and Wilds (29). A solution of 5.4 g. (0.02 mole) of V in 20 ml. of dry, thiophene-free benzene was swirled and cooled in ice-water while 5.2 g. of phosphorus pentachloride was added in portions. After swirling the mixture for 10 minutes at room temperature, both compounds dissolved and the solution turned yellow. After another 5 minutes in the ice bath, the solution was cooled in a mixture of dry-ice and acetone until it began to solidify, and 5 ml. of anhydrous stannic chloride dissolved in 5 ml. of benzene was added in one portion. Upon mixing, an orange complex separated, and after swirling the mixture in the ice bath for 10 minutes the complex was decomposed by the addition with stirring of a mixture of ice and 10 ml. of concentrated hydrochloric acid. Stirring was continued until decomposition was complete. The ketone was collected, washed with dilute acid, dilute base, and finally with water, and recrystallized from ethanol, to yield 4.1 g. (75%) melting at 176-178° (6).

1,2,3,4-Tetrahydronaphtho[2,3-*b*]benzothiophene.

This compound was prepared by the reduction of VI using the Wolff-Kishner procedure, as described for V. The yield after recrystallization from ethanol was 83%, m.p. 112-114° (7,8).

1,2,3,4-Tetrahydronaphtho[2,3-*b*]benzothiophene 7,7-dioxide.

This sulfone was obtained in 90% yield by the hydrogen peroxide-acetic acid oxidation procedure (17), and melted at 190-190.5°.

Anal. Calcd. for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22; S, 11.86. Found: C, 71.13; H, 5.22; S, 11.44.

Naphtho[2,3-*b*]benzothiophene (IIa).

Prepared by dehydrogenation of the tetrahydro derivative with palladium-on-charcoal, by the method described for Ia, the product melted at 160.5-161° (7,8). One g. of the tetrahydro derivative yielded only 0.4 g. of IIa.

Naphtho[2,3-*b*]benzothiophene 5,5-dioxide.

The sulfone of IIa, recrystallized from ethanol, melted at 267-268°.

Anal. Calcd. for $C_{16}H_{10}O_2S$: C, 72.16; H, 3.79. Found: C, 71.97; H, 3.99.

Naphtho[1,2-*b*]benzothiophene (IIIa).

Using the method of Rabindran and Tilak (10), 2-(α-naphthylmercapto)cyclohexanone was cyclized with phosphorus pentoxide to produce 7,8,9,10-tetrahydronaphtho[1,2-*b*]benzothiophene, m.p. 98.5-99°, in 61% yield. This compound is reported to melt at 97-98° (10). Its picrate melted at 141.5-142°, and was previously reported to melt at 137-138° (10). Oxidation with hydrogen peroxide in acetic acid gave white crystalline 7,8,9,10-tetrahydronaphtho[1,2-*b*]benzothiophene 11,11-dioxide, melting at 224-226°.

Anal. Calcd. for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22. Found: C, 70.94; H, 5.23.

Dehydrogenation of the tetrahydronaphthobenzothiophene over palladium-on-charcoal, as described above, produced 80% of IIIa, melting at 182-184°, as previously reported (10). Oxidation of a portion of this product in the usual way produced a crystalline sulfone, melting at 232-234°.

Anal. Calcd. for $C_{16}H_{10}O_2S$: C, 72.16; H, 3.79. Found: C, 72.32; H, 3.84.

8,9,10,11-Tetrahydronaphtho[2,1-*b*]benzofuran.

This compound was prepared directly without isolation of the intermediate hemiacetal (19). Fourteen and four-tenths g. of 2-naphthol (0.1 mole), 13.2 g. (0.1 mole) of 2-chlorocyclohexanone, 50 ml. of 95% ethanol and 13.8 g. (0.1 mole) of potassium carbonate were combined and refluxed until carbon dioxide ceased to be evolved, about 1.5 hours. The salts were removed by filtration and washed with ethanol. Filtrate and washings were then combined and treated with a solution of 22.9 g. (0.1 mole) of picric acid dissolved in 150 ml. of ethanol. This mixture was heated to the boiling point and then allowed to cool overnight in the refrigerator. The picrate was collected by filtration and the filtrate was concentrated to approximately 50 ml. to obtain a second crop of crystals. The total yield of crude product, melting at 139-141° was 28.1 g. (62.5%). The picrate was dissolved in the minimum amount of acetone and added drop-wise with rapid stirring to 800 ml. of 28% ammonia solution. Stirring was continued for 30 minutes after addition was complete. The crystals which separated were collected by filtration, washed thoroughly with water, and dried, giving 13.5 g. (61%) of product melting at 45-45.5°, as previously reported (19).

Naphtho[2,1-*b*]benzofuran, (Ib).

A 50 ml. round-bottom flask was fitted with a condenser to the top of which was attached a tube leading to a small column. The column, clamped vertically, was filled with 100-150 g. of chlorinated lime. In the flask were placed 4.40 g. (0.02 mole) of 8,9,10,11-tetrahydronaphtho[2,1-*b*]benzofuran and an excess (4.0 g., 0.05 mole) of powdered selenium. The flask was then heated on a bath of Wood's metal until hydrogen selenide was evolved at 345-360°, as evidenced by the red coloration of the bleaching powder. After about one and one-half hours evolution of hydrogen selenide ceased and the flask was cooled and the contents extracted throughly with several portions of boiling ethanol. The extracts were filtered with Norite A, and upon concentration, a clear oil appeared which crystallized after cooling and scratching the flask with a stirring rod. Upon recrystallization from ethanol, 3.2 g. (75%) of pure product was obtained which melted at 42.5-43°. Both Osdene and Russell (19) and Chatterjea (30) reported this compound to melt at 31-32°.

However, the ultraviolet spectrum and melting point of a picrate (125.3-125.8°) are in agreement with those reported (19), and a mixture m.p. with starting material (m.p. 45-45.5°) was depressed to 30-33°.

7,8,9,10-Tetrahydronaphtho[1,2-*b*]benzofuran.

A three-necked flask equipped with stirrer and condenser was swept out with nitrogen and in it were placed 28.8 g. (0.20 mole) of 1-naphthol (redistilled, m.p. 95-96°), 26.4 g. (0.20 mole) of chlorocyclohexanone, 150 ml. of 95% ethanol, and 27 g. of anhydrous potassium carbonate. The mixture was refluxed under nitrogen until all carbon dioxide evolution ceased (approximately 2 hours) and poured into 1 l. of cold water. The aqueous mixture was extracted with three 200 ml. portions of ether, and the extracts were combined, washed thoroughly with water, dried over anhydrous sodium sulfate, and the ether removed at reduced pressure.

The residue was fractionally distilled at 0.5 mm. The first fraction, collected below 100°, weighed 7.6 g. and consisted of chlorocyclohexanone. The second fraction, collected at 102-106° proved to be unchanged 1-naphthol and weighed 13.5 g. (47% of the starting material). A third fraction was collected as a yellow, viscous oily mixture between 160 and 225°, which solidified on standing, and melted from 38-50°. The crude product weighed 9.2 g. Upon recrystallization from ethanol, 4.1 g. (9.2%) of pure white product melting at 81-82° was obtained; ν max (potassium bromide), 1170 (aryl C-O), 1140 (cyclic ether) cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.48; H, 6.35. Found: C, 86.13; H, 6.33.

A picrate was prepared by the usual procedure, crystallized from ethanol, and melted at 133-133.2°.

Anal. Calcd. for $C_{22}H_{17}O_8N_3$: C, 58.54; H, 3.80. Found: C, 58.12; H, 3.60.

Naphtho[1,2-*b*]benzofuran (IIIb).

A mixture of 1.11 g. (5 mmoles) of 7,8,9,10-tetrahydro-[1,2-*b*]benzofuran and 1.5 g. powdered selenium was heated at 360° until hydrogen selenide evolution ceased (approximately 2.5 hours). The mixture was cooled, extracted with hot ethanol, and the extracts were treated with Norite A. Upon concentration of the extracts to 10 ml., and cooling, 0.82 g. (76%) of white needles separated which melted at 102-102.5°, as previously reported (20).

Anal. Calcd. for $C_{16}H_{10}O$: C, 88.05; H, 4.62. Found: C, 87.67; H, 4.70.

REFERENCES

(1) Contribution No. 1503. This work was supported in part by a research grant (C-1948 (C)) from the National Cancer Institute of the National Institutes of Health, Public Health Service.

(2) Taken in part from a thesis submitted by S. W. O. for the degree Doctor of Philosophy at Indiana University, 1962.

(3) F. G. Bordwell, W. H. McKellin and D. Babcock, *J. Am. Chem. Soc.*, 73, 5566 (1951).

(4) F. Mayer, *Ann. Chem.*, 488, 259 (1931).

(5) O. Kruber and L. Rappen, *Chem. Ber.*, B73, 1184 (1940).

(6) H. Gilman and A. L. Jacoby, *J. Org. Chem.*, 3 108 (1938).

(7) N. P. Buu-Hoi and P. Cagniant, *Chem. Ber.*, B76, 1269 (1943).

(8) E. G. G. Werner, *Rec. Trav. Chim.*, 68, 520 (1949).

(9) K. Rabindran and B. D. Tilak, *Current Sci.* (India), 20, 207 (1951).

(10) K. Rabindran and B. D. Tilak, *Proc. Indian Acad. Sci.*, 37A, 564 (1953).

(11) E. B. McCall has indicated in a patent (*Chem. Abstr.*, 49, 4027d (1955)) that this condensation goes equally well in the presence of aqueous sodium hydroxide.

(12) The boiling point of 1,2,3,4-tetrahydrodibenzothiophene was reported by Rabindran and Tilak (9) as 141°/10 mm. and confirmed by us (140°/10 mm. or 115-119°/0.7 mm.) and by McCall (*Chem. Abstr.*, 49, 4027d (1955)). However, Buu-Hoi and Cagniant (7), who prepared this compound by succinoylation of benzothiophene, followed by Clemmensen reduction and ring closure to 4-ketotetrahydrodibenzothiophene, and finally further Clemmensen reduction to tetrahydrodibenzothiophene, reported a boiling point of 180°/3 mm. Because of the possibility of rearrangement of such ketones during Clemmensen reduction, the tetrahydro compound was prepared by both methods and the two compounds were found to be identical, as shown by a mixed melting point of their picrates.

(13) Provided through the courtesy of Professor F. G. Bordwell, Northwestern University.

(14) Huang-Minlon, *J. Am. Chem. Soc.*, 68, 2487 (1946).

(15) R. A. Robinson and E. Mosettig, *ibid.*, 61, 1148 (1939).

(16) K. Rabindran and B. D. Tilak, *Proc. Indian Acad. Sci.*, 37A, 557 (1953).

(17) F. G. Bordwell, B. B. Lampert and W. H. McKellin, *J. Am. Chem. Soc.*, 71, 1702 (1949).

(18) We are indebted to Dr. E. Mosettig, of the National Institutes of Health, for a sample of this compound.

(19) T. S. Osdene and P. B. Russell, *J. Org. Chem.*, 31, 2646 (1966).

(20) J. N. Chatterjea, *Experientia*, 12, 18 (1956).

(21) The ultraviolet absorption curves shown in Figures 1 and 2 were obtained from 95% ethanol solution of compounds Ia and b, IIa and b and IIIa and b in 1.00 cm. silica cells on a Beckmann DK-1 double-beam recording spectrophotometer.

(22) G. M. Badger and B. J. Christie, *J. Chem. Soc.*, 3438, (1956), reported the identical U. V. spectra of compounds IIb and IIIb, among other tetranuclear heterocyclic systems.

(23) M. Orchin and R. A. Friedel, *J. Am. Chem. Soc.*, 71, 3002 (1949).

(24) G. R. Clemo and D. G. I. Felton, *J. Chem. Soc.*, 1658 (1952).

(25) A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy", 2nd Ed., Arnold, London, 1958, p. 137.

(26) All melting points are corrected. Microanalyses are by Miss Joanna Dickey of this department.

(27) A. L. Wilds and W. S. Johnson, *J. Am. Chem. Soc.*, 68, 87 (1946).

(28) G. D. Johnson, *ibid.*, 73, 5888 (1951).

(29) W. E. Bachman and A. L. Wilds, *ibid.*, 62, 2084 (1940).

(30) J. N. Chatterjea, *J. Indian Chem. Soc.*, 33, 339 (1956).

Received August 5, 1968 Bloomington, Indiana 47401