The Synthesis of Naphtho[1,2-*b*]thiophene and All of the Eight Isomers of Monomethylnaphtho[1,2-*b*]thiophene

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The synthesis of naphtho[1,2-*b*]thiophene and all of the eight monomethylnaphtho[1,2-*b*]thiophene isomers is described.

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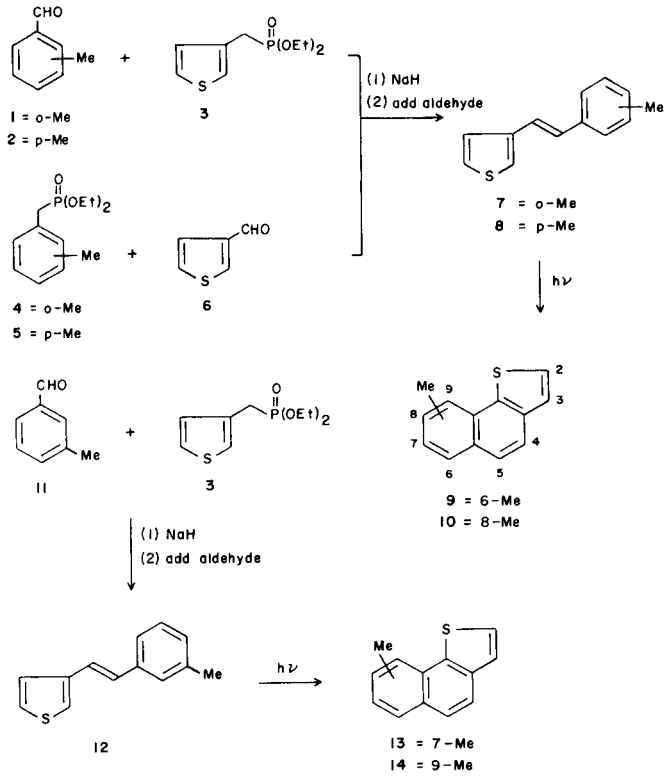
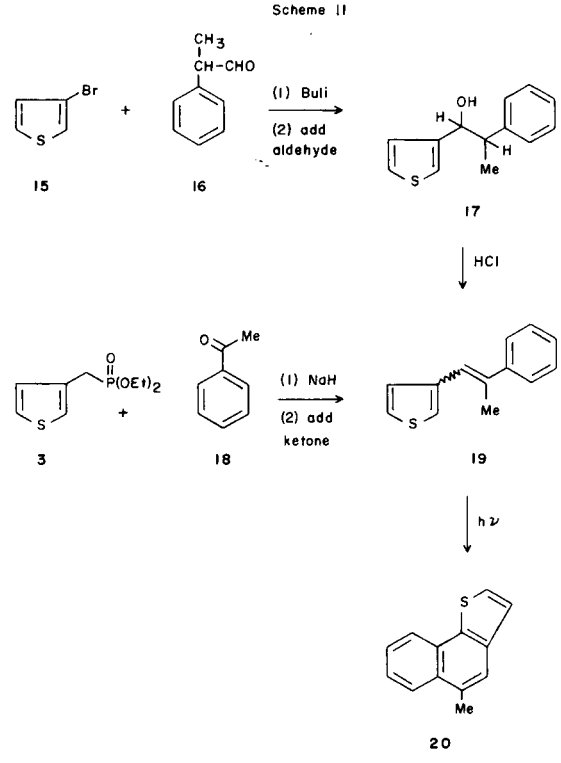
Willey, Iwao, Castle and Lee [3] observed a peak of 184 *via* gas chromatography-mass spectrometry in two different coal liquids (SRC-I and SRC-II) and also in both Paraho and Livermore shale oils. The peak was assigned to the parent naphtho[1,2-*b*]thiophene. Thus it was necessary to synthesize an authentic specimen of naphtho[1,2-*b*]thiophene (**30**) and also it was of interest to synthesize all of the eight monomethyl isomers of naphtho[1,2-*b*]thiophene in order to verify their presence in coal liquids, shale oils and coal derived products. This is a continuation of our program [4-23] directed toward the synthesis of all of the potentially mutagenic unsubstituted polycyclic thiophenes and their monomethyl, dimethyl and monoethyl derivatives which occur or are suspected of occurring in coal liquids and related coal-derived products.

2-Methylbenzaldehyde (**1**) or 4-methylbenzaldehyde (**2**) when allowed to react at room temperature for four hours with diethyl 3-thenylphosphonate (**3**) [4] in the presence of sodium hydride and 1,2-dimethoxyethane gave 3-(2′-methylstyryl)thiophene (**7**) in 73% yield or 3-(4′-methylstyryl)-thiophene (**8**) in 78% yield respectively. The colorless needles of **7** or the pale yellow crystals of **8** were also obtained from the condensation of thiophene-3-carboxaldehyde (**6**) with diethyl 2-methylbenzylphosphonate (**4**) in 80% yield or diethyl 4-methylbenzylphosphonate (**5**) in 85% yield respectively. The configuration of the above

Scheme I



Scheme II



alkenes and all of the alkenes which follow is unknown. The configuration of the alkenes is unimportant because they are all intermediates in the photocyclization reaction.

Photocyclization of **7** or **8** with a 450 watt medium pressure Hanovia mercury lamp for five hours gave 6-methylnaphtho[1,2-*b*]thiophene (**9**) in 46% yield or 8-methylnaphtho[1,2-*b*]thiophene (**10**) in 42% yield respectively.

When 3-methylbenzaldehyde (**11**) was allowed to react with phosphonate **3** [4] under Wadsworth-Emmons conditions, 3-(3'-methylstyryl)thiophene (**12**) was obtained in 70% yield as silver flakes. Compound **12** gave two products upon photocyclization, namely, 7-methylnaphtho-[1,2-*b*]thiophene (**13**) and 9-methylnaphtho[1,2-*b*]thiophene (**14**) which were separated by column chromatography on a basic alumina column using hexane and benzene as eluents. 9-Methylnaphtho[1,2-*b*]thiophene (**14**) eluted first using pure hexane as the eluent in 13% yield. It was obtained as a pale yellow oil. Upon further elution with hexane:benzene (2:1), 7-methylnaphtho[1,2-*b*]thiophene (**13**) was obtained in 15% yield as an oil (Scheme I). The structural assignments of the 7-methyl isomer **13** and the 9-methyl isomer **14** were based upon their nmr spectra. In **14** the methyl signal (δ 3.00) is more deshielded than the methyl signal in **13** (δ 2.52) due to the ring current effect.

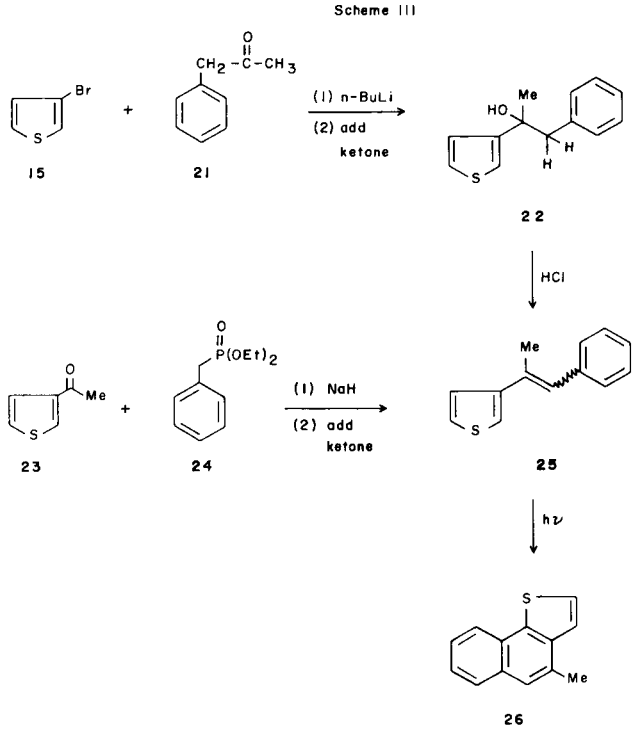
The reaction of 3-bromothiophene (**15**) with *n*-butyllithium at −78° gave the lithio derivative which was immediately allowed to react with 2-phenylpropanal (**16**) to give the alcohol **17**. The crude alcohol **17**, which was only characterized spectrally, was dehydrated with concentrated hydrochloric acid to give 2-phenyl-1-(3-thienyl)propene (**19**) in 65% yield from compound **15**. The pale yellow flakes of **19** were also obtained in 45% yield from the condensation of diethyl 3-thenylphosphonate (**3**) [4] with acetophenone (**18**).

Photocyclization of **19** gave 5-methylnaphtho[1,2-*b*]thiophene (**20**) [24] in 39% yield (Scheme II). Compound **20** was previously prepared by a different method [24].

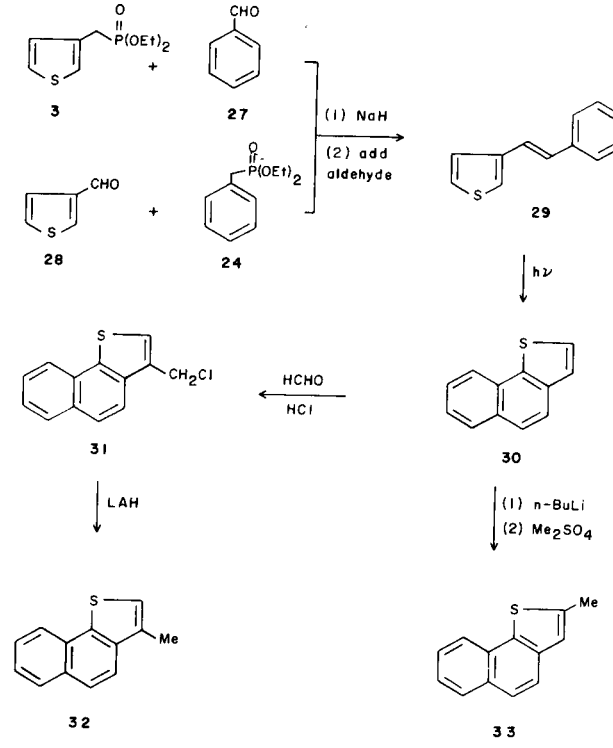
Reaction of 3-lithiothiophene with phenylacetone (**21**) gave the alcohol **22** as a pale yellow oil. The crude alcohol **22**, which was only characterized spectrally, was dehydrated with concentrated hydrochloric acid to give 1-phenyl-2-(3-thienyl)propene (**25**) in 70% yield from compound **15**. The pale yellow needles of **25** were also obtained by the Wadsworth-Emmons reaction of 3-acetylthiophene with diethyl benzylphosphonate (**24**) in 46% yield. Photocyclization of **25** gave 4-methylnaphtho[1,2-*b*]thiophene (**26**) in 37% yield (Scheme III).

3-Styryl thiophene (**29**) was prepared in 78% yield from diethyl 3-thenylphosphonate (**3**) [4] with benzaldehyde (**27**) and also in 73% yield from thiophene-3-carboxaldehyde (**28**) and diethyl benzylphosphonate (**24**) under Wadsworth-Emmons conditions. The colorless leaflets of **29** were photocyclized for 5 hours to give naphtho[1,2-*b*]thiophene (**30**) [25,26] in 42% yield as a pale yellow oil. From the parent compound **30** we obtained the two monomethyl isomers, namely, 3-methylnaphtho[1,2-*b*]thiophene (**32**) and 2-methylnaphtho[1,2-*b*]thiophene (**33**). When naphtho[1,2-*b*]thiophene (**30**) [25,26] was treated with formaldehyde and hydrogen chloride, 3-chloromethylnaphtho-

Scheme III



Scheme IV



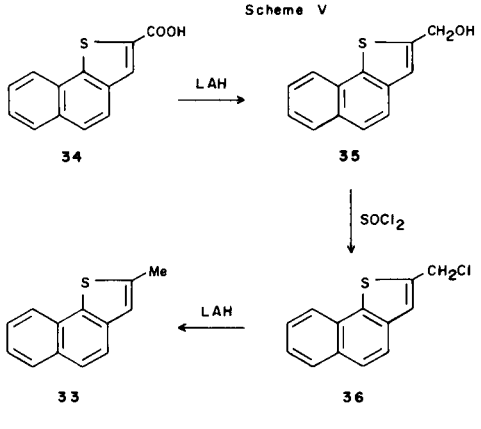
[1,2-*b*]thiophene (**31**) was obtained in 70% yield. Reduction of **31** with lithium aluminum hydride gave 3-methylnaphtho[1,2-*b*]thiophene (**32**) [27,28] in 90% yield. Compound **32** was previously prepared by different methods by Clarke *et al.* [27] and by Knapp [28].

It is well known that naphtho[1,2-*b*]thiophene (**30**) [25,26] lithiates at position two [26,27]. When the 2-lithio derivative was allowed to react with dimethyl sulfate, 2-methylnaphtho[1,2-*b*]thiophene (**33**) [24,27] was obtained in 73% yield (Scheme IV). Compound **33** was previously prepared by different methods (Cagniant *et al.* [24] and Clarke *et al.* [27]).

2-Methylnaphtho[1,2-*b*]thiophene (**33**) [24,27] was also obtained in three steps from naphtho[1,2-*b*]thiophene-2-carboxylic acid (**34**) [27]. Upon treatment with lithium aluminum hydride compound **34** gave 2-hydroxymethylnaphtho[1,2-*b*]thiophene (**35**) as colorless crystals in 91% yield. When compound **35** was allowed to react with thionyl chloride, 2-chloromethylnaphtho[1,2-*b*]thiophene (**36**) was obtained in 77% yield. 2-Methylnaphtho[1,2-*b*]thiophene (**33**) [24,27] was obtained in 89% yield by reduction of the chloro compound **36** with lithium aluminum hydride.

Some of the monomethyl derivatives of naphtho[1,2-*b*]-thiophene are being screened against TA-98 and TA-100 in the Ames test (S9 liver homogenate activation) and these results will be published elsewhere.

Scheme V



EXPERIMENTAL

Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. The ir spectra were obtained on a Beckmann Acculab 2 spectrometer. The ^{1}H-nmr spectra were obtained on a Varian EM-360A spectrometer in the solvents indicated using TMS as the internal standard. Chemical shifts are reported in δ units. Mass spectra were obtained on a Hewlett-Packard model 5980A mass spectrometer. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona.

3-(2'-Methylstyryl)thiophene (**7**). Method A.

Sodium hydride (50% dispersion in mineral oil, 1.1 g, 0.045 mole) was placed in dry 1,2-dimethoxyethane (120 ml). Sodium hydride was used after washing twice with hexane (60 ml). The slurry was cooled to 20° and diethyl 3-thenylphosphonate (**3**) (2.58 g, 0.011 mole) [4] was added with stirring under a stream of nitrogen. After the addition, the solution was stirred at room temperature for 15 minutes. To the pale yellow solution maintained below 25°, 2-methylbenzaldehyde (**1**) (1.32 g, 0.011 mole) was slowly added *via* a syringe. The solution was stirred at room temperature for 3.5 hours. The reaction mixture was slowly poured into a large excess of ice-water and the resulting precipitate was collected by filtration. The product was recrystallized from methanol affording colorless needles in 73% yield (1.61 g), mp 96-97°.

Method B.

Compound **7** was prepared from diethyl 2-methylbenzylphosphonate (**4**) (2.33 g, 0.011 mole) and thiophene-3-carboxaldehyde (**6**) (1.23 g, 0.011 mole) in a manner similar to the preparation of compound **7**, Method A, and 1.76 g (80%) of colorless needles was obtained, mp 96-97°; nmr (deuteriochloroform): δ 2.32 (s, C*H*$_3$, 3H), 6.96-7.59 (m, 2 × ethenyl-*H*, and aromatic-*H*, 7H); ms: m/e 200 (M$^+$, 100).

Anal. Calcd. for $C_{13}H_{12}S$: C, 77.95; H, 6.04; S, 16.01. Found: C, 77.89; H, 5.90; S, 16.23.

3-(4'-Methylstyryl)thiophene (**8**). Method A.

Compound **8** was prepared from diethyl 3-thenylphosphonate (**3**) (2.58 g, 0.011 mole) [4] and 4-methylbenzaldehyde (**2**) (1.32 g, 0.011 mole) in a manner similar to the preparation of compound **7** and pale yellow crystals were obtained in 78% yield (1.72 g), mp 123-124°.

Method B.

Compound **8** was prepared from diethyl 4-methylbenzylphosphonate (**5**) (2.33 g, 0.011 mole) and thiophene-3-carboxaldehyde (**6**) (1.23 g, 0.011 mole) in a manner similar to the preparation of compound **7** and pale yellow crystals were obtained in 85% yield (1.87 g), mp 123-124°; nmr (deuteriochloroform): δ 2.33 (s, C*H*$_3$, 3H), 6.87-7.44 (m, 2 × ethenyl-*H* and aromatic *H*, 7H); ms: m/e 200 (M$^+$, 100).

Anal. Calcd. for $C_{13}H_{12}S$: C, 77.95; H, 6.04; S, 16.01. Found: C, 78.10; H, 6.20; S, 15.83.

6-Methylnaphtho[1,2-*b*]thiophene (**9**).

A solution of 3-(2'-methylstyryl)thiophene (**9**) (1.1 g, 0.0055 mole) and iodine (0.05 g) in benzene (360 ml) was irradiated for five hours with a 450 watt Hanovia medium pressure mercury lamp. During the course of the reaction a slow stream of air was passed through the solution. The solvent was evaporated *in vacuo* and the residue was chromatographed on a neutral alumina column using hexane:benzene (2:1) as the eluent affording a pale yellow oil in 46% yield (0.5 g); nmr (deuteriochloroform): δ 2.67 (s, C*H*$_3$, 3H), 7.02-8.22 (m, 7H, Ar*H*); ms: 198 (M$^+$, 100).

Anal. Calcd. for $C_{13}H_{10}S$: C, 78.75; H, 5.08; S, 16.17. Found: C, 78.64; H, 5.12; S, 16.23.

8-Methylnaphtho[1,2-*b*]thiophene (**10**).

This compound was obtained by photocyclizing 3-(4'-methylstyryl)thiophene (**8**) (1.1 g, 0.0055 mole) in a manner similar to the preparation of compound **9**. Compound **10** was obtained as a pale yellow oil in 42% yield (0.46 g); nmr (deuteriochloroform): δ 2.50 (s, C*H*$_3$, 3H), 7.02-8.09 (m, 7H and Ar*H*, 9H); ms: m/e 198 (M$^+$, 100).

Anal. Calcd. for $C_{13}H_{10}S$: C, 78.75; H, 5.08; S, 16.17. Found: C, 78.70; H, 5.12; S, 16.28.

3-(3'-Methylstyryl)thiophene (**12**).

3-(3'-Methylstyryl)thiophene (**12**) was synthesized from diethyl 3-thenylphosphonate (**3**) (2.58 g, 0.011 mole) and 3-methylbenzaldehyde (**11**) (1.32 g, 0.011 mole) in a similar manner to the preparation of compound **7**. The silver flakes of **12** were obtained in 70% yield (1.54 g), mp 75-76°; nmr (deuteriochloroform): δ 2.30 (s, C*H*$_3$, 3H), 6.84-7.48 (m, 2 × ethenyl-*H*, aromatic *H*, 7H); ms: m/e 200 (M$^+$, 100).

Anal. Calcd. for $C_{13}H_{12}S$: C, 77.95; H, 6.04; S, 16.01. Found: C, 77.88; H, 5.89; S, 15.87.

7-Methylnaphtho[1,2-*b*]thiophene (**13**) and 9-Methylnaphtho[1,2-*b*]thiophene (**14**).

Compounds **13** and **14** were obtained from compound **12** (1.3 g, 0.0065 mole) and iodine (0.05 g) in a similar manner to the preparation of

6-methylnaphtho[1,2-*b*]thiophene (**9**). The residue obtained after five hours of photocyclization was chromatographed on a basic alumina column using hexane and benzene as the eluents. Compound **14** eluted first in pure hexane and upon further elution with hexane:benzene (2:1) pure **13** was obtained.

Compound **13**.

This compound was obtained as a pale yellow oil in 15% yield (0.2 g); nmr (deuteriochloroform): δ 2.52 (s, C*H*$_3$, 3H), 7.00-7.92 (m, 7H and Ar*H*, 7H); ms: m/e 198 (M$^+$, 100).

Anal. Calcd. for $C_{13}H_{10}S$: C, 78.75; H, 5.08; S, 16.17. Found: C, 78.63; H, 4.83; S, 16.33.

Compound **14**.

Compound **14** was obtained as a pale yellow oil in 13% yield (0.17 g); nmr (deuteriochloroform): δ 3.00 (s, C*H*$_3$, 3H), 7.03-8.08 (m, 7H, Ar*H*); ms: m/e 198 (M$^+$, 100).

Anal. Calcd. for $C_{13}H_{10}S$: C, 78.75; H, 5.08; S, 16.17. Found: C, 78.83; H, 5.19; S, 16.39.

3-(α-Methylstyryl)thiophene (**19**). Method A.

Compound **19** was obtained from diethyl 3-thenylphosphonate (**3**) (2.3 g, 0.011 mole) [4] and acetophenone (**18**) (1.39 g, 0.011 mole) in a manner similar to the preparation of compound **7** and pale yellow flakes were obtained in 45% yield (1.0 g), mp 58-59°.

Method B.

Compound **17**.

3-Bromothiophene (**15**) (16.3 g, 0.1 mole) in 400 ml of dry ether was placed in 1000 ml three-neck flask with an addition funnel, thermometer and a drying tube as an inlet for dry nitrogen. The solution was cooled to −78° in an acetone dry-ice bath and *n*-butyllithium (1.6 *M*, 75 ml, 0.12 mole) was added dropwise. After the addition the mixture was stirred for 1.5 hours at −20 to −10° and for 2 hours at room temperature. The mixture was then cooled to −70° and 2-phenylpropanal (13.4 g, 0.1 mole) in 50 ml of dry ether was added dropwise. After the addition, the solution was allowed to warm to 25° and was stirred for an additional 5 hours. The ether solution was poured into 250 ml of 15% hydrochloric acid solution and the mixture was extracted with 2 × 150 ml portions of chloroform. The chloroform layer was dried over anhydrous sodium sulfate and evaporated *in vacuo* to give compound **17** as a pale yellow oil; nmr (deuteriochloroform): δ 2.43 (bs, O*H*, 1H), 3.05 (m, -C*H*-CH$_3$, 1H), 4.89 (d, J = 7 Hz, =C*H*-OH, 1H), 6.68-7.14 (m, 8H, Ar*H*).

Compound **19**.

A mixture of the above crude alcohol **17** and 200 ml of concentrated hydrochloric acid solution was refluxed for 2 hours and then the reaction mixture was extracted with benzene. The benzene layer was dried over anhydrous sodium sulfate and evaporated *in vacuo* to give a brown oil. The crude product was chromatographed on a silica gel column using hexane as the eluent affording pale yellow flakes in 65% yield (13 g, from compound **15**), mp 60°; nmr (deuteriochloroform): δ 2.33 (s, C*H*$_3$, 3H), 6.89-7.52 (m, 2 × ethenyl-*H* and aromatic *H*, 8H); ms: m/e 200 (M$^+$, 100).

Anal. Calcd. for $C_{13}H_{12}S$: C, 77.95; H, 6.04; S, 16.01. Found: C, 77.83; H, 6.23; S, 16.29.

5-Methylnaphtho[1,2-*b*]thiophene (**20**).

Compound **20** [24] was obtained in a 39% yield from the photocyclization of compound **19** (1.2 g, 0.0060 mole). The pale yellow oil (0.46 g) obtained had nmr (deuteriochloroform): δ 2.62 (s, C*H*$_3$, 3H), 7.20-7.55 (m, H-2, H-3, H-7, H-8, 4H, Ar*H*), 7.50 (s, H-4, 1H, Ar*H*), 7.80-8.20 (m, H-6, H-9, 2H, ArH); ms: m/e 198 (M$^+$, 100).

Anal. Calcd. for $C_{13}H_{10}S$: C, 78.75; H, 5.08; S, 16.17. Found: C, 79.01; H, 5.00; S, 15.89.

1-Phenyl-2-(3-thienyl)propene (**25**). Method A.

Compound **25** was prepared from 3-acetylthiophene (**23**) (1.39 g, 0.011 mole) and diethyl benzylphosphonate (**24**) (2.33 g, 0.011 mole) in a manner similar to the preparation of compound **7** and pale yellow needles were obtained in 46% yield (1.01 g), mp 63-64°.

Method B.

Compound **22**.

The reaction of 3-bromothiophene (**15**) (16.3 g, 0.1 mole) and phenylacetone (**21**) (13.4 g, 0.1 mole) in a manner similar to the preparation of **17** gave a pale yellow oil; ir (potassium bromide): 3450 cm^{-1} (OH).

Compound **25**.

This compound was prepared by the dehydration of compound **22** in a similar manner to the preparation of compound **19** Method B. The pale yellow needles were obtained in 70% yield (13.9 g, from compound **15**), mp 66°; nmr (deuteriochloroform): δ 2.60 (s, C*H*$_3$, 3H), 7.18-7.65 (m, 2 × ethenyl-*H* and aromatic-*H*, 8H); ms: m/e 200 (M$^+$, 100).

4-Methylnaphtho[1,2-*b*]thiophene (**26**).

Compound **25** (1.1 g, 0.0055 mole) was irradiated with a 450 watt medium pressure Hanovia mercury lamp for five hours in a similar manner to the preparation of 6-methylnaphtho[1,2-*b*]thiophene (**9**) affording 0.40 g (37%) of a pale yellow oil; nmr (deuteriochloroform): δ 2.58 (s, C*H*$_3$, 3H), 7.12-7.90 (m, 7H, Ar*H*); ms: m/e 198 (M$^+$, 100).

Anal. Calcd. for $C_{13}H_{10}S$: C, 78.75; H, 5.08; S, 16.17. Found: C, 78.72; H, 5.13; S, 15.99.

3-Styrylthiophene (**29**). Method A.

3-Styrylthiophene (**29**) was prepared under Wadsworth-Emmons conditions from diethyl 3-thenylphosphonate (**3**) (4.9 g, 0.024 mole) [4] and benzaldehyde (**27**) (2.6 g, 0.024 mole) in a manner similar to the preparation of **7** and colorless leaflets were obtained in 78% yield (3.5 g), mp 123-124°.

Method B.

Compound **29** was prepared from the condensation of thiophene-3-carboxaldehyde (**28**) (4.2 g, 0.037 mole) and diethyl benzylphosphonate (**24**) (7.9 g, 0.037 mole) in a similar manner to the preparation of compound **7** and colorless leaflets were obtained in 73% yield (5.1 g), mp 123-124°; nmr (deuteriochloroform): δ 6.83-7.68 (m, 2 × ethenyl-*H* and aromatic-*H*, 8H); ms: m/e 186 (M$^+$, 100).

Anal. Calcd. for $C_{12}H_{10}S$: C, 77.49; H, 5.41; S, 17.21. Found: C, 77.38; H, 5.38; S, 17.39.

Naphtho[1,2-*b*]thiophene (**30**).

The parent compound **30** [25,26] was obtained from the photocyclization of 3-styrylthiophene (**29**) in a similar manner to the preparation of compound **9**. Purification was done by neutral alumina column chromatography using hexane as the eluent affording a colorless oil which solidified upon standing becoming colorless leaflets, mp 29-30° (lit mp 27-28° [25]); nmr (deuteriochloroform): δ 7.16-8.19 (m, 8H, ArH); ms: m/e 184 (M$^+$, 100).

3-Chloromethylnaphtho[1,2-*b*]thiophene (**31**).

A rapid stream of hydrogen chloride was passed into a vigorously stirred mixture of 37% aqueous formaldehyde (1.0 g, 0.013 mole), concentrated hydrochloric acid (1.1 g, 0.013 mole) and naphtho[1,2-*b*]thiophene (**30**) (2.3 g, 0.013 mole) [25,26] until the mixture was saturated. The temperature was maintained at 65 to 70° during the course of the reaction for two hours while a slow stream of hydrogen chloride was passed into the reaction mixture. After cooling, 350 ml of cold water was added. The organic layer was separated and the aqueous layer extracted twice with 80 ml portions of benzene. The organic layer and extracts were combined, washed many times with water and saturated sodium bicarbonate solution, and then dried over anhydrous sodium sulfate and evaporated *in vacuo* affording a light brown oil which crystallized upon standing. Purification was achieved by recrystallization from methanol affording colorless needles in 70% yield (1.76 g), mp 149-150°; nmr (deuteriochloroform): δ 4.75 (s, C*H*$_2$Cl, 2H), 6.92-7.95 (m, 7H, Ar*H*); ms: m/e 232 (M$^+$, 23), 197 (M$^+$ − 35, 100).

Anal. Calcd. for $C_{13}H_9ClS$: C, 67.09; H, 3.90; S, 13.78. Found: C, 67.14; H, 4.03; S, 13.55.

3-Methylnaphtho[1,2-*b*]thiophene (**32**).

Lithium aluminum hydride (0.69 g, 0.019 mole) was added to a suspension of 3-chloromethylnaphtho[1,2-*b*]thiophene (**31**) (1.2 g, 0.0061 mole) in dry ether (100 ml). The reaction mixture was stirred at room temperature for 4 hours under nitrogen and then quenched by cautiously adding water (20 ml) and enough 15% hydrochloric acid to dissolve the inorganic salts. The mixture was poured into ice-water and extracted twice with 150 ml portions of benzene. The extracts were washed with water and saturated sodium bicarbonate solution, dried over anhydrous sodium sulfate and evaporated *in vacuo*. The residue was chromatographed on a silica gel column using hexane:benzene (2:1) as the eluent affording colorless crystals in 90% yield (1.2 g), mp 61-62° (lit mp 62-68 [27] and 60.5-61.5° [28]); nmr lit [27]; ms: m/e 198 (M^+, 100).

2-Methylnaphtho[1,2-*b*]thiophene (**33**). Method A.

Naphtho[1,2-*b*]thiophene (**30**) (1.5 g, 0.0081 mole) [25-26] in dry ether (100 ml) was placed in a 300 ml three neck flask with a thermometer and a drying tube serving as an inlet for dry nitrogen. The solution was then coooled to −78° in a dry-ice acetone bath. *n*-Butyllithium solution (1.6 *M* in hexane, 7.5 ml, 0.010 mole) was slowly added *via* a syring. After the addition, the mixture was stirred for one hour at −20° and for an additional 4 hours at room temperature. The mixture was then cooled to −50 to −60° and dimethyl sulfate (1.26 g, 0.010 mole) in 20 ml of dry ether was added dropwise. After the addition, the solution was allowed to warm to 25° and it was stirred for an additional 16 hours. The reaction mixture was poured into a 15% cold hydrochloric acid solution and the mixture extracted twice with 100 ml portions of chloroform. The chloroform layer was dried over anhydrous sodium sulfate and evaporated *in vacuo*. The residue was chromatographed on a neutral alumina column using hexane:benzene (2:1) as the eluent affording a pale yellow oil in 73% yield.

Method B.

Compound **33** was prepared from compound **36** (1.0 g, 0.0043 mole) and lithium aluminum hydride (0.58 g, 0.016 mole) in a manner similar to the preparation of compound **32** and pale yellow oil was obtained in 89% yield (0.76 g); nmr (deuteriochloroform): δ 2.54 (s, C*H*$_3$, 3H), 6.86-8.12 (m, 7H, Ar*H*); ms: m/e 198 (M^+, 100). This compound was previously prepared *via* different synthetic methods (Cagniant *et al.* [24] and Clarke *et al.* [27]).

2-Hydroxymethylnaphtho[1,2-*b*]thiophene (**35**).

Compound **35** was prepared from naphtho[1,2-*b*]thiophene-2-carboxylic acid (**34**) (3.0 g, 0.012 mole) [37] and lithium aluminum hydride (0.8 g, 0.022 mole) in a similar manner to the preparation of compound **32** and colorless crystals were obtained in 91% yield (2.28 g), mp 159-160°; nmr (deuteriochloroform): δ 2.68 (bs, O*H*, 1H), 4.68 (s, C*H*$_2$, 2H), 6.99-8.12 (m, 7H, Ar*H*); ms: m/e 214 (M^+, 100), 215 ($M^+ + 1$), 197 (95).

Anal. Calcd. for $C_{13}H_{10}OS$: C, 72.87; H, 4.70; S, 14.96. Found: C, 72.74; H, 4.82; S, 15.08.

2-Chloromethylnaphtho[1,2-*b*]thiophene (**36**).

A mixture of compound **35** (2.0 g, 0.0093 mole) thionyl chloride (3.0 ml, 0.025 mole) and dry benzene (100 ml) was refluxed for 2 hours. After removal of the benzene and the excess thionyl chloride *in vacuo*, the residue was chromatographed on a silica gel column using benzene as the eluent affording pale yellow crystals in 77% yield (1.7 g), mp 158-160° An analytical sample was prepared by recrystallization from methanol affording colorless crystals, mp 163-164°; nmr (deuteriochloroform): δ 4.81 (s, C*H*$_2$, 2H), 6.92-8.11 (m, 7H, Ar*H*); ms: m/e 232 (M^+, 22), 197 ($M^+ - 35$, 100).

Anal. Calcd. for $C_{13}H_9ClS$: C, 67.09; H, 3.90; S, 13.78. Found; C, 66.88; H, 3.73; S, 13.93.

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