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Cyclohepta[*cd*]benzothiophene **3**, a new heterocyle, was synthesized starting from benzothiophene *via* eight steps in 14% total yield. Chemical reactions of **3** were examined on formylation, acetylation, bromination, catalytic hydrogenation and Diels-Alder reactions. The results show that the benzothiophene moiety of **3** has aromatic character and the carbon-carbon double bonds in a seven-membered ring posseses alkene-like character.

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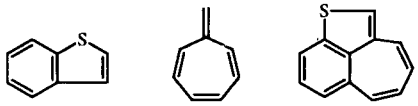
Introduction.

Benzothiophene **1** is a typical heterocyclic compound which posseses aromatic character. Halogenation [1], acylation [2], nitration [3] and alkylation [4] occur predominantly at the 3-position of benzothiophene. When the 3-position is substituted the reactions occur at the 2-position. Lithiation of benzothiophene **1** with butyllithium affords 2-benzothienyllithium which give a variety of products [5]. In contrast, heptafulvene **2** is known as a nonbenzenoid compound which form a stable tropyrium ion with acids [6]. However, the four carbon-carbon double bonds in heptafulvene is easily hydrogenated [6a] and have alkene-like charcter rather than aromatic character. Combination of benzothiophene and heptafulvene give a new heterocyclic system, cyclohepta[*cd*]benzothiophene **3**. We are interested in the synthesis and properties of cyclohepta[*cd*]benzothiophene **3**.



1 **2** **3**

Figure 1

There are a few literature examples which report cyclohepta[*cd*]benzothiophene derivatives. For example, Royer *et al.* [7] prepared 2-ethylcyclohepta[*cd*]benzothiophene **6** starting from 2-ethylbenzothiophene **4**. Neidlein *et al.* [8] also synthesized compound **5** from **4** and bromo derivative **8** from **7**.

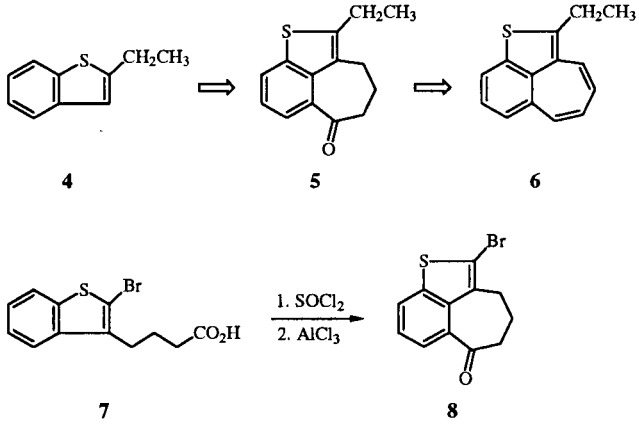
Results and Discussion.

We planned the synthesis of the fundamental molecule **3** of cyclohepta[*cd*]benzothiophene derivatives according to the procedures of Royer and Neidlein. The synthetic pathways are summarized in Scheme 2.

Benzothiophene **1** reacted with ethyl 3-(chloroformyl)-propionate in the presence of tin(IV) chloride in benzene to give methyl 3-(3-benzothenoyl)propionate **9** in 81% yield [8]. Wolff-Kishner reduction of **9** using hydrazine hydrate and sodium hydroxide produced 4-(3-benzothienyl)butyric acid **10** in 87% yield [8]. Protection of the 2-position in the benzothiophene ring of **10** is necessary because intramolecular cyclization of **10** affords the six-membered ketone **13** rather than the seven-membered ketone **12**. Therefore, compound **10** was chlorinated with chlorine to give 4-(2-chloro-3-benzothienyl)butyric acid **11**. However, it was difficult to isolate **11** in a pure state because a small amount of the dichloro compound and starting material were included. Compound **11** was used without further purification for the following step. Bromination [8] of **10** using bromine is convenient compared with chlorination, however, the bromine atom is easily cleaved during next intramolecular cyclization to give the six-membered ring ketone **13**. Cyclization of **11** with polyphosphoric acid [7a] gave a mixture of 2-chloro-3,4,5,6-tetrahydrocyclohepta[*cd*]benzothiophen-6-one **12** (53%) and 1,2,3,4-tetrahydrobenzothiophen-6-one **13** (13%).

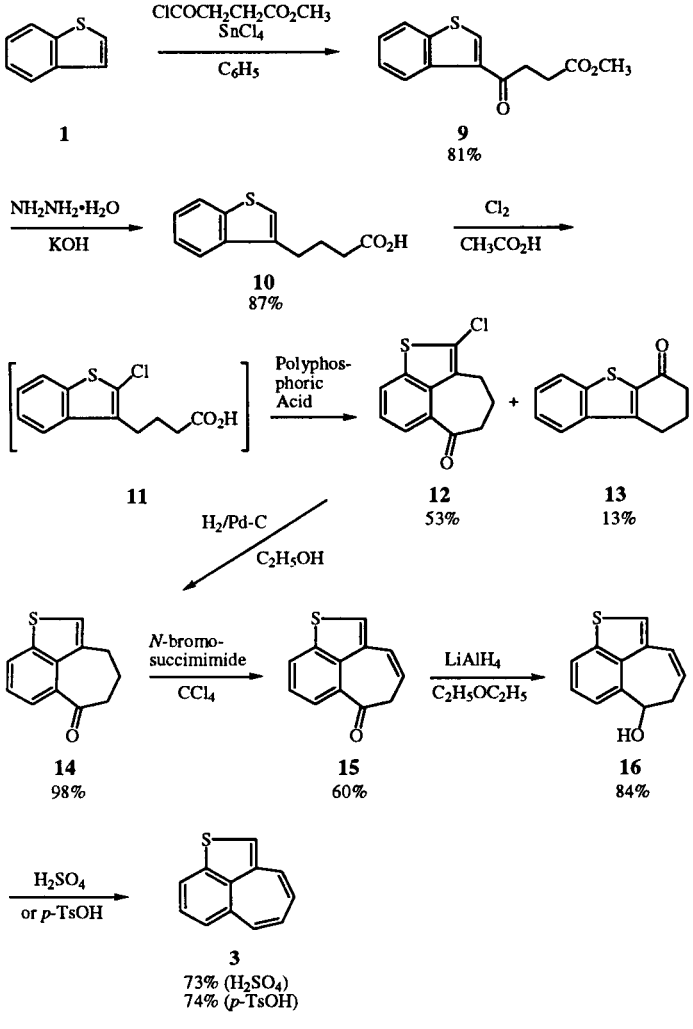
Dechlorination [9] of **12** proceeded smoothly by catalytic hydrogenation with 7% palladium-charcoal to give 3,4,5,6-tetrahydrocyclohepta[*cd*]benzothiophen-6-one **14** in 98% yield. To introduce carbon-carbon double bonds

Scheme 1



4 **5** **6** **7** **8**

Scheme 2



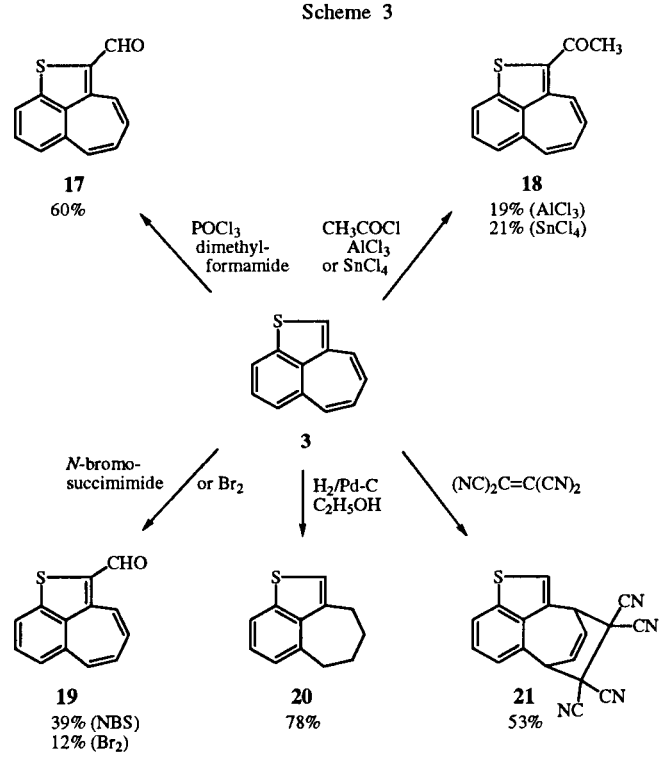
into the seven-membered ring, **14** was treated with *N*-bromosuccinimide in the presence of benzoyl peroxide. The product was 5,6-dihydrocyclohepta[*cd*]benzothiophen-6-one **15** which was produced by bromination followed by elimination of hydrogen bromide. The carbonyl group of **15** was reduced with lithium aluminum hydride to afford 5,6-dihydrocyclohepta[*cd*]benzothiophen-6-ol **16** in 84% yield. Finally, when alcohol **16** was heated with 25% sulfuric acid in ethanol, the desired cyclohepta[*cd*]benzothiophene **3** was obtained in 73% yield. When *p*-toluenesulfonic acid was used instead of sulfuric acid in benzene, **3** was obtained in 74% yield. The total yield of cyclohepta[*cd*]benzothiophene from benzothiophene **1** was 14%.

Cyclohepta[*cd*]benzothiophene **3** was obtained as red crystals from acetone-water, mp 88.5-89° and is stable in air at room temperature. The structure of **3** was determined from the ^1H and ^{13}C nmr spectra. Four protons on the seven-membered ring of **3** appear at alkene region of 5.15-5.46 (m, 2H) and 5.77-6.06 ppm (m, 2H). In contrast, one proton on thiophene ring of **3** appears at 6.43 ppm (s, 1H) and three protons on the benzene ring of **3** at 6.45 (d, J = 8 Hz, 1H), 6.83 (dd, J = 8 and 8 Hz, 1H) and 7.19 ppm (d, J = 8 Hz, 1H). These three protons are in the aromatic region. The ^{13}C nmr spectrum supports the structure of **3**. In benzoheptafulvene, similar four protons on the seven-membered ring appear at a little lower magnetic field of 5.70-6.80 ppm [10]. Similarly, six protons of benzothiophene are at lower magnetic field of 7.26-7.90 ppm. The results suggest that carbon-carbon double bonds in the seven-membered ring of **3** have alkene-like character and the benzothiophene moiety of **3** posseses aromatic character.

Next, we examined chemical properties of **3** using Vilsmeier-Haack formylation, Friedel-Crafts acetylation, bromination, catalytic hydrogenation and the Diels-Alder reaction. Formylation and acetylation are typical reactions of aromatic compounds and catalytic hydrogenation and Diels-Alder reaction are characteristic reactions of alkene compounds.

First, when cyclohepta[*cd*]benzothiophene **3** was heated with phosphoryl chloride in *N,N*-dimethylformamide, 2-formylcyclohepta[*cd*]benzothiophene **17** was obtained in 60% yield, showing high reactivity at the 2-position. In the case of benzothiophene **1**, 2-formylbenzothiophene is prepared by the reaction of 2-benzothienyllithium and methylformanilide [5c]. Acetylation of **3** with acetyl chloride and anhydrous aluminum chloride [2a] or tin(IV) chloride [2c] produced 2-acetylcyclohepta[*cd*]benzothiophene **18** in 19

Scheme 3



and 21% yields, respectively. Bromination with *N*-bromosuccinimide or bromine [1b-d] occured at the 2-position to give 2-bromocyclohepta[*cd*]benzothiophene **19** in 39 and 12% yields, respectively. The results show that the 2-position of **3** is reactive toward to electrophilic reagents and has aromatic character like benzothiophene.

Secondly, properties of the heptafulvene moiety were examined. Catalytic hydrogenation of **3** with palladium-charcoal proceeded smoothly to give 3,4,5,6-tetrahydrocyclohepta[*cd*]benzothiophene **20** in 78% yield. In this case, the carbon-carbon double bond in the thiophene ring was not reduced. In the case of heptafulvene, all four double bonds are reduced by catalytic hydrogenation to methylcycloheptane [6a]. Protonation of **3** with trifluoroacetic acid was attempted, however, a stable tropyrium ion [6,11] which is a typical property of heptafulvene was not formed. The Diels-Alder reaction of **3** with tetracyanoethylene occured to give adduct **21** in 53% yield. Two double bonds in the seven-membered ring of **3** reacted as a diene. The Diels-Alder reaction of **3** with other dienophiles such as dimethyl acetylenedicarboxylate, maleic anhydride or *p*-benzoquinone did not occur. In genreral, [8+2] cycloaddition [6] occurs in the Diels-Alder reaction of heptafulvenes, however, [4+2] cycloaddition [6b] also occurs in substituted heptafulvene. Thus, carbon-carbon double bonds in the seven-membered ring exhibit alkene-like character.

From the above results, cyclohepta[*cd*]benzothiophene **3** posseses both the characters of benzothiophene and heptafulvene.

EXPERIMENTAL

The melting points are uncorrected. Column chromatography was performed on silica gel (Wakogel C-200). Unless otherwise stated anhydrous sodium sulfate was employed as the drying agent. Ether refers to diethyl ether. The ir spectra were determined on a Hitachi Model 270-30 IR spectrometer. The ^1H and ^{13}C nmr spectra were determined at 90 MHz and 22.49 MHz on a JEOL-FX 90Q FT NMR sectrometer, using tetramethylsilane as the internal standard.

Methyl 3-(3-Benzothenoyl)propionate **9**.

Tin(IV) chloride (406 g, 1560 mmoles) was added dropwise over 30 minutes with stirring at 0° to a mixture of benzothiophene **1** (60.0 g, 447 mmoles) and methyl 3-(chloroformyl)propionate (90.0 g, 598 mmoles) dissolved in dry benzene (360 ml). The mixture was stirred for 4 hours at 0°, and then kept for 20 hours at room temperature. The mixture was decomposed with ice (420 g) and concentrated hydrochloric acid (360 ml) and extracted with benzene. The extract was washed with a 5% sodium hydroxide solution, then with water and dried. Evaporation of the extract gave **9** (90.1 g, 81%). It formed colorless crystals from methanol, mp 94-95° ([8] mp 96°); ir (potassium bromide): 1730 (CO_2CH_3), 1662 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.79 (t, J = 7 Hz, 2H, $COCH_2CH_2$), 3.34 (t, J = 7 Hz, 2H, $COCH_2CH_2$), 3.71 (s, 3H, OCH_3), 7.20-7.54 (m, 2H, Ar-H_2), 7.74-7.96 (m, 1H, Ar-H), 8.33 (s, 1H, C_2-H), 8.62-8.76 (m, 1H, Ar-H); ^{13}C nmr (deuteriochloroform): δ 28.0 (t), 34.7 (t), 51.7 (q), 122.2 (d), 125.4 (d), 125.5 (d), 125.8 (d), 134.7 (s), 136.5 (s), 136.8 (d), 139.7 (s), 173.2 (s), 193.0 (s).

Anal. Calcd. for $C_{13}H_{12}O_3S$: C, 62.88; H, 4.87. Found: C, 62.67; H, 5.02.

4-(3-Benzothienyl)butyric Acid **10**.

A mixture of **9** (20.0 g, 80.5 mmoles), powdered sodium hydroxide (26.0 g, 650 mmoles), hydrazine hydrate (26.8 g, 535 mmoles) and diethyleneglycol (325 ml) was refluxed for 2 hours. The water produced and an excess of hydrazine hydrate were removed by distillation off and then the mixture was refluxed for 3 hours. Ice and 6*M* hydrochloric acid were added to the mixture until the solution became acidic. The resulting product was extracted with ether. The extract was washed, dried and evaporated to give **10** (15.4 g, 87%). It formed colorless crystals from benzene, mp 108.5-109° ([8] mp 108-111°); ir (potassium bromide): 1685 cm^{-1} (CO_2H); ^1H nmr (deuteriochloroform): δ 1.87-2.29 (m, 2H, $CH_2CH_2CH_2CO_2H$), 2.46 (t, J = 7 Hz, 2H, $CH_2CH_2CH_2CO_2H$ or $CH_2CH_2CH_2CO_2H$), 2.91 (t, J = 7 Hz, 2H, $CH_2CH_2CH_2CO_2H$ or $CH_2CH_2CH_2CO_2H$), 7.10 (s, 1H, C_2-H), 7.17-7.47 (m, 2H, Ar-H_2), 7.60-7.89 (m, 2H, Ar-H_2), 10.85 (broad s, 1H, CO_2H); ^{13}C nmr (deuterioacetone): δ 25.3 (t), 28.3 (t), 33.7 (t), 122.4 (d), 122.5 (d), 123.5 (d), 124.7 (d), 124.9 (d), 137.0 (s), 139.8 (s), 141.3 (s), 174.7 (s).

Anal. Calcd. for $C_{12}H_{12}O_2S$: C, 65.43; H, 5.49. Found: C, 65.58; H, 5.64.

2-Chloro-3,4,5,6-tetrahydrocyclohepta[*cd*]benzothiophen-6-one **12** and 1,2,3,4-Tetrahydrodibenzothiophen-4-one **13**.

Chlorine gas was prepared from potassium permanganate (5.00 g, 31.6 mmoles) and 6*M* hydrochloric acid (50 ml). The chlorine was introduced with stirring at room temperature to afford **10** (10.0 g, 45.5 mmoles) in 90% acetic acid (250 ml) by passing nitrogen for 2 hours. The mixture was poured into water and kept overnight. The resulting precipitate was filtered, washed and dried. The chlorinated product **11** was used directly without purification for the following step.

A mixture of **11** (10.0 g) and polyphosphoric acid (1000 g) was heated at 85° under stirring for 7 hours. The mixture was poured into ice-water and extracted with ether. The extract was washed with a 5% sodium hydroxide solution, then with water, dried and evaporated. The residue was chromatographed and eluted with benzene. The first fraction gave **12** (5.70 g, 53%). It formed colorless crystals from benzene, mp 69-70°; ir (potassium bromide): 1655, 1665 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 1.96-2.28 (m, 2H, $CH_2CH_2CH_2$), 2.88-3.16 (m, 4H, $CH_2CH_2CH_2$), 7.38 (dd, J = 8 and 8 Hz, 1H, C_8-H), 7.85 (dd, J = 1 and 8 Hz, 1H, C_9-H), 8.06 (dd, J = 1 and 8 Hz, 1H, C_7-H); ^{13}C nmr (deuteriochloroform): δ 21.1 (t), 29.6 (t), 45.3 (t), 123.9 (d), 126.4 (d), 127.5 (d), 128.8 (s), 132.1 (s), 133.3 (s), 135.7 (s), 138.3 (s), 199.8 (s).

Anal. Calcd. for $C_{12}H_9ClOS$: C, 60.89; H, 3.83. Found: C, 60.72; H, 3.94.

The second fraction afforded **13** (1.20 g, 13%). It formed colorless crystals from benzene, mp 66-67°; ir (potassium bromide): 1650 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.04-2.40 (m, 2H, $CH_2CH_2CH_2CO$), 2.68 (t, J = 6 Hz, 2H, $CH_2CH_2CH_2CO$ or $CH_2CH_2CH_2CO$), 2.97 (t, J = 6 Hz, 2H, $CH_2CH_2CH_2CO$ or $CH_2CH_2CH_2CO$), 7.18-7.50 (m, 2H, Ar-H_2), 7.56-7.90 (m, 2H, Ar-H_2); ^{13}C nmr (deuteriochloroform): δ 23.9 (t), 24.0 (t), 38.5

(t), 123.4 (d), 123.7 (d), 124.7 (d), 127.9 (d), 136.2 (s), 138.2 (s), 142.4 (s), 147.7 (s), 193.3 (s).

Anal. Calcd. for $C_{12}H_{10}OS$: C, 71.24; H, 4.98. Found: C, 71.12; H, 5.12.

3,4,5,6-Tetrahydrocyclohepta[*cd*]benzothiophen-6-one **14**.

A mixture of **12** (5.00 g, 21.1 mmoles), triethylamine (3.35 g, 33.1 mmoles), 7% palladium-charcoal (1.00 g) and ethanol (100 ml) was shaken under a hydrogen atomosphere at room temperature for 3 hours. After filtration of the catalyst the ethanol was evaporated. The residue was extracted with ether. The extract was washed with 1*M* hydrochloric acid, then with water, dried and evaporated. The residue was chromatographed and eluted with benzene to give **14** (4.20 g, 98%). It formed colorless crystals from benzene, mp 51-52°; ir (potassium bromide): 1660 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 1.96-2.26 (m, 2H, $CH_2CH_2CH_2CO$), 3.07 (t, J = 7 Hz, 2H, $CH_2CH_2CH_2CO$ or $CH_2CH_2CH_2CO$), 3.13 (t, J = 7 Hz, 2H, $CH_2CH_2CH_2CO$ or $CH_2CH_2CH_2CO$), 7.21 (s, 1H, C_2-H), 7.38 (dd, J = 8 and 8 Hz, 1H, C_8-H), 7.94 (dd, J = 1 and 8 Hz, 1H, C_9-H), 8.02 (dd, J = 1 and 8 Hz, 1H, C_7-H); ^{13}C nmr (deuteriochloroform): δ 22.0 (t), 31.5 (t), 45.7 (t), 123.5 (d), 123.6 (d), 126.7 (d), 127.3 (d), 133.0 (s), 136.3 (s), 137.0 (s), 141.8 (s), 200.8 (s).

Anal. Calcd. for $C_{12}H_{10}OS$: C, 71.25, H, 4.98. Found: C, 71.20; H, 5.10.

5,6-Dihydrocyclohepta[*cd*]benzothiophen-6-one **15**.

A mixture of **14** (1.00 g, 4.94 mmoles), *N*-bromosuccinimide (0.966 g, 5.43 mmoles), benzoyl peroxide (0.066 g, 0.272 mmole) and tetrachloromethane (400 ml) was refluxed for 1.5 hours. After cooling, water was added to the mixture, and it was stirred at room temperature for 1.5 hours. The mixture was extracted with ether. The extract was washed, dried and evaporated. The residue was chromatographed and eluted with benzene to give **15** (0.594 g, 60%). It formed colorless crystals from benzene-hexane, mp 58.5-59°; ir (potassium bromide): 1670 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 3.54 (dd, J = 1 and 7 Hz, 2H, C_5-H_2), 5.84 (dt, J = 11 and 7 Hz, 1H, C_4-H), 6.74 (d, J = 11 Hz, 1H, C_3-H), 7.41 (dd, J = 8 and 8 Hz, 1H, C_8-H), 7.44 (s, 1H, C_2-H), 7.90 (d, J = 8 Hz, 1H, C_7-H or C_9-H), 7.98 (d, J = 8 Hz, 1H, C_7-H or C_9-H); ^{13}C nmr (deuteriochloroform): δ 45.0 (t), 120.9 (d), 124.1 (d), 125.4 (d), 126.3 (d), 126.8 (d), 128.1 (d), 134.9 (s), 135.0 (s), 135.2 (s), 141.1 (s), 192.8 (s).

Anal. Calcd. for $C_{12}H_8OS$: C, 71.97; H, 4.03. Found: C, 72.14; H, 4.06.

5,6-Dihydrocyclohepta[*cd*]benzothiophen-6-ol **16**.

Compound **15** (0.500 g, 2.50 mmoles) in dry ether (43 ml) was added dropwise during 10 minutes with stirring at 0° to a dry ethereal solution (63 ml) of lithium aluminum hydride (0.035 g, 0.922 mole). The mixture was stirred for 10 minutes at 0° and decomposed with water. The mixture was extracted with ether. The extract was washed with 2*M* hydrochloric acid, then with water, dried and evaporated. The residue was chromatographed and eluted with benzene-ether 8:2, to give **16** (0.424 g, 84%). It formed colorless crystals from benzene-hexane, mp 67-68°; ir (potassium bromide): 3300 cm^{-1} (OH); ^1H nmr (deuteriochloroform): δ 2.06 (s, 1H, OH), 2.56-3.14 (m, 2H, C_5-H_2), 5.08 (dd, J = 2 and 7 Hz, 1H, C_6-H), 5.64-5.92 (m, 1H, C_4-H), 6.79 (dd, J = 2 and 11 Hz, 1H, C_3-H), 7.18-7.40 (m, 2H, C_7-H and C_8-H), 7.39 (s, 1H, C_2-H), 7.80 (dd, J = 3 and 7 Hz, C_9-H); ^{13}C nmr (deuteriochloroform): δ 36.5 (t), 72.0 (d), 122.4 (d), 123.5 (d), 123.8 (d), 124.5 (d), 126.0 (d), 127.1 (d), 134.1 (s), 135.1 (s), 140.2 (s), 141.7 (s).

Anal. Calcd. for $C_{12}H_{10}OS$: C, 71.25; H, 4.98. Found: C, 71.16; H, 5.07.

Cyclohepta[*cd*]benzothiophene **3**.

Method A.

Sulfuric acid (30 ml, 25%) was added to an ethanolic solution (60 ml) of **16** (0.150 g, 0.742 mmole) and the mixture was heated at 100° for 1 hour. After cooling, ice-water (300 ml) was poured into the solution. The mixture was extracted with ether. The extract was washed, dried and evaporated. The residue was chromatographed and eluted with hexane to give **3** (0.100 g, 73%). It formed red crystals from acetone-water, mp 88.5-89°; ^1H nmr (deuteriochloroform): δ 5.00-5.44 (m, 2H, C_4-H and C_5-H), 5.64-6.08 (m, 2H, C_3-H and C_6-H), 6.43 (s, 1H, C_2-H), 6.45 (d, J = 8 Hz, 1H, C_7-H or C_9-H), 6.83 (dd, J = 8 and 8 Hz, 1H, C_8-H), 7.19 (d, J = 8 Hz, 1H, C_7-H or C_9-H); ^{13}C nmr (deuteriochloroform): δ 119.2 (d), 122.5 (d), 123.5 (d), 125.0 (d), 126.0 (d), 127.7 (d), 131.6 (d), 135.2 (d), 137.6 (s), 139.5 (s), 142.0 (s), 143.6(s).

Anal. Calcd. for $C_{12}H_8S$: C, 78.22; H, 4.38. found: C, 78.08; H, 4.51.

Method B.

A mixture of **16** (0.430 g, 2.13 mmoles), *p*-toluenesulfonic acid (0.005 g, 0.029 mmole) and benzene (100 ml) was refluxed for 1 hour. The solution was washed, dried and evaporated. The residue was chromatographed and eluted with hexane to give **3** (0.291 g, 74%).

2-Formylcyclohepta[*cd*]benzothiophene **17**.

Phosphoryl chloride (0.102 g, 0.665 mmole) in *N,N*-dimethylformamide (0.2 ml) was added to compound **3** (30.0 mg, 0.163 mmole) dissolved in *N,N*-dimethylformamide (1.7 ml). The solution was heated at 80° under stirring for 2 hours. After cooling, the solution was poured into ice-water and kept overnight. The solution was extracted with ether. The extract was washed, dried and evaporated. The residue was chromatographed and eluted with benzene to give **17** (21.0 mg, 60%). It formed red crystals from benzene-hexane, mp 137-138°; ir (potassium bromide): 1640 cm^{-1} (CHO); ^1H nmr (deuteriochloroform): δ 5.60-5.92 (m, 2H, C_4-H and C_5-H), 6.11-6.35 (m, 1H, C_6-H), 6.75 (d, J = 7 Hz, 1H, C_7-H or C_9-H), 6.88-7.25 (m, 1H, C_3-H), 7.14 (dd, J = 7 and 7 Hz, 1H, C_8-H), 7.38 (d, J = 7 Hz, 1H, C_7-H or C_9-H), 10.05 (s, 1H, CHO).

Anal. Calcd. for $C_{13}H_8OS$: C, 73.56; H, 3.80. Found: C, 73.40; H, 3.95.

2-Acetylcyclohepta[*cd*]benzothiophene **18**.

Compound **3** (30.0 mg, 0.163 mmole) in dichloromethane (10 ml) was dropped at 0° to a dichloromethane solution (2 ml) of acetyl chloride (32.0 mg, 0.408 mmole) and aluminum chloride (55.0 mg, 0.412 mole). The mixture was stirred at 0° for 2 hours and poured into a saturated sodium hydrogen carbonate solution. The mixture was extracted with dichloromethane. The extract was washed, dried and evaporated. The residue was chromatographed and eluted with benzene to give **18** (7.0 mg, 19%) and unreacted **3** (16 mg, 53%). It formed red crystals from benzene-hexane, mp 58-59°; ir (potassium bromide): 1658 cm^{-1} ($COCH_3$); ^1H nmr (deuteriochloroform): δ 2.49 (s, 3H, $COCH_3$), 5.58-5.92 (m, 2H, C_4-H and C_5-H), 6.08-6.34 (m, 1H, C_6-H), 6.75 (d, J = 7 Hz, 1H,

C_7-H or C_9-H), 7.13 (dd, J = 7 and 7 Hz, 1H, C_8-H), 7.32 (d, J = 7 Hz, 1H, C_7-H or C_9-H), 7.48-7.72 (m, 1H, C_3-H).

Anal. Calcd. for $C_{14}H_{10}OS$: C, 74.31; H, 4.45. Found: C, 74.20: H, 4.58.

2-Bromocyclohepta[*cd*]benzothiophene **19**.

Method A.

Bromine (29.0 mg, 0.363 mmole) in tetrachloromethane (3 ml) was added dropwise at 0° to **3** (30.0 mg, 0.163 mmole) dissolved in tetrachloromethane (3 ml). The solution was stirred at 0° for 2 hours. After evaporation of the solvent, the residue was chromatographed and eluted with hexane to give **19** (5.0 mg, 12%). It formed red crystals from benzene-hexane, mp 39-40°; ^{1}H nmr (deuteriochloroform): δ 5.20-5.52 (m, 2H, C_4-H and C_5-H), 5.70-6.22 (m, 2H, C_3-H and C_6-H), 6.49 (d, J = 7 Hz, 1H, C_7-H or C_9-H), 6.90 (dd, J = 7 and 7 Hz, 1H, C_8-H), 7.11 (d, J = 7 Hz, 1H, C_7-H or C_9-H).

Anal. Calcd. for $C_{12}H_7BrS$: C, 54.77; H, 2.68. Found: C, 54.62; H, 2.80.

Method B.

A mixture of **3** (30.0 mg, 0.163 mmole), *N*-bromosuccinimide (29.0 mg, 0.163 mmole), benzoyl peroxide (2.0 mg, 0.028 mmole) and tetrachloromethane (12 ml) was refluxed for 2 hours. After evaporation of the solvent, the residue was chromatographed and eluted with hexane to give **19** (17.0 mg, 39%).

3,4,5,6-Tetrahydrocyclohepta[*cd*]benzothiophene **20**.

A mixture of **3** (30.0 mg, 0.163 mmole), 7% palladium-charcoal (50.0 mg) and ethanol (5 ml) was shaken under hydrogen atomosphere for 2 hours at room temperature. After removal of the catalyst by filtration, the ethanol was evaporated. The residue was chromatographed and eluted with hexane to give **20** (24.0 mg, 78%). It formed colorless crystals from acetone-water, mp 41.5-42°; ^{1}H nmr (deuteriochloroform): δ 1.74-2.24 (m, 4H, C_4-H_2 and C_5-H_2), 2.84-3.18 (m, 4H, C_3-H_2 and C_6-H_2), 6.92 (s, 1H, C_2-H), 6.96 (d, J = 7 Hz, 1H, C_7-H or C_9-H), 7.16 (dd, J = 7 and 7 Hz, 1H, C_8-H), 7.62 (d, J = 7 Hz, 1H, C_7-H or C_9-H).

Anal. Calcd. for $C_{12}H_{12}S$: C, 76.55; H, 6.42. found: C, 76.58; H, 6.52.

Adduct **21**.

A mixture of **3** (30.0 mg, 0.163 mmole), tetracyanoethylene (24.0 mg, 0.187 mmole) and benzene (5 ml) was refluxed for 2 hours. After evaporation of the benzene, the residue was chromatographed and eluted with benzene to give **21** (25.0 mg, 53%). It formed colorless crystals from acetone-hexane, mp 196-198°; ir (potassium bromide): 2250 cm^{-1} (CN); ^{1}H nmr (deuterioacetone): δ 4.98-5.10 (m, 1H, C*H*CH=CHCH), 5.16-5.28 (m, 1H, CHCH=CHC*H*), 6.68-7.04 (m, 2H, CH=CH), 7.30-7.64 (m, 2H, Ar-H_2), 8.03 (s, 1H, thiophene-H), 8.06 (dd, J = 2 and 7 Hz, 1H, Ar-H).

Anal. Calcd. for $C_{16}H_8N_4S$: C, 66.65, H, 2.80, N, 19.43. Found: C, 66.47; H, 3.01; N, 19.24.

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