Furan Derivatives. Part 10 [1]. Synthesis of Cyclohepta[*cd*]benzofuran

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Cyclohepta[*cd*]benzofuran **2** was synthesized by heating (5-oxo-5*H*-benzocyclohepten-4-yloxy)acetic acid **16** with sodium acetate in acetic anhydride or by photocyclization of **16** in acetonitrile. Several reactions of cyclohepta[*cd*]benzofuran **2** were examined. Protonation of **2** with trifluoroacetic acid occurred at the 2-position to give a tropylium ion **17**. Catalytic hydrogenation of **2** with palladium on charcoal proceeded smoothly to give tetrahydrocyclohepta[*cd*]benzofuran **18**. The Diels-Alder reaction of **2** with tetracyanoethylene produced an adduct **19**. Formylation of **2** with phosphorus oxychloride and dimethylformamide occurred easily at the 2-position to afford compound **20**. Cyclohepta[*cd*]benzofuran **2** has both properties of heptafulvene and benzofuran.

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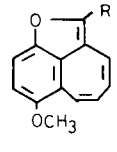
Introduction.

Heptafulvene [2,3] and benzoheptafulvene [4,5] are well-known nonbenzenoid compounds which form a stable tropylium ion [3-5,6] with acids. However, the double bonds in heptafulvene have olefinic character rather than aromatic character [7]. On the other hand, benzofuran is a typical aromatic heterocyclic compound and the double bond in the furan ring has aromatic character [8]. Cyclohepta[*cd*]benzofuran **2** has both the structures of heptafulvene and benzofuran in the molecule. Therefore, the properties of cyclohepta[*cd*]benzofuran are interesting. In the previous paper [1], we reported synthesis and several reactions of 7-methoxycyclohepta[*cd*]benzofuran **1**. In the present paper, we synthesize a parent compound of cyclohepta[*cd*]benzofuran **2** and examine its chemical properties to compare with those of 7-methoxycyclohepta[*cd*]benzofuran **1a**, heptafulvene, or benzofuran.



a ; R = H
b ; R = CH_3
c ; R = C_2H_5
d ; R = CO_2H
e ; R = CHO
f ; R = $COCH_3$

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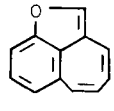

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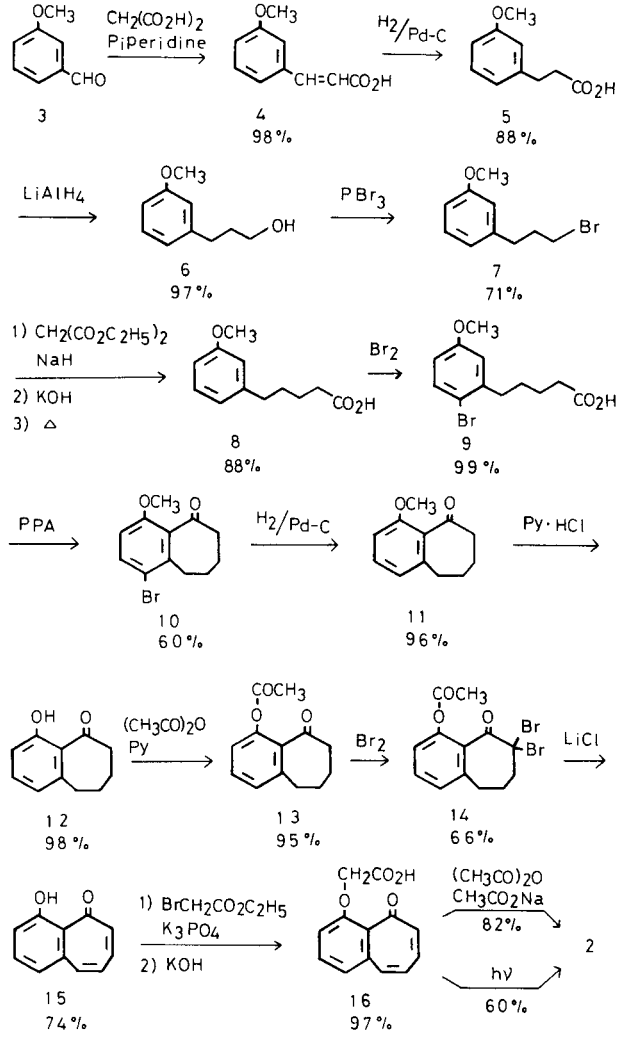
Results and Discussion.

Cyclohepta[*cd*]benzofuran **2** was synthesized through fourteen steps starting from *m*-anisaldehyde **3**. The synthetic pathway of **2** is summarized in Scheme 1.

When *m*-anisaldehyde was condensed with malonic acid in the presence of piperidine, 3-(3-methoxyphenyl)propenoic acid **4** was obtained in 98% yield [9,10]. The acid **4** was readily hydrogenated to 3-(3-methoxyphenyl)propionic

Scheme 1

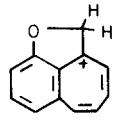


acid **5** in 88% yield using palladium on charcoal as a catalyst [11]. For preparation of seven-membered cyclic ketone, it was necessary to extend the carbon side-chain of **5**. The acid **5** was initially reduced with lithium aluminum hydride to give 3-(3-methoxyphenyl)propan-1-ol **6** in 97% yield [12]. The alcohol **6** was then converted to 1-(3-bromopropyl)-3-methoxybenzene **7** in 71% yield with phosphorus tribromide [12]. To extend the carbon side-chain, the bromide **7** was allowed to react with diethyl malonate in the presence of sodium hydride. After hydrolysis of the ester by potassium hydroxide the resulting dicarboxylic acid was heated at 190° for decarboxylation to give 5-(3-methoxyphenyl)pentanoic acid **8** in 88% yield [12]. The acid **8** was also synthesized by condensation of *m*-anisaldehyde **3** with methyl crotonate in the presence of potassium *t*-butoxide followed by hydrolysis of the ester and catalytic hydrogenation of the carbon-carbon double bonds with Raney nickel [13]. Benzyltrimethylammonium chloride is often used as a base in the condensation reaction [14,15].

The acid **8** was brominated [16] with bromine to avoid an unfavorable cyclization reaction in the next step [16]. The bromination proceeded smoothly to give 5-(2-bromo-5-methoxyphenyl)pentanoic acid **9** in 99% yield. When the acid **9** was treated with polyphosphoric acid (PPA), 1-bromo-4-methoxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one **10** was obtained in 60% yield [17,18]. A large amount of polyphosphoric acid is necessary to increase the yield of seven-membered cyclic ketone. When the ketone **10** was hydrogenated using palladium on charcoal as a catalyst, the bromine atom was readily removed [16] to give 5-methoxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one **11** in 96% yield. The demethylation reaction [19] of **11** by heating with pyridinium chloride at 200° afforded 5-hydroxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one **12** in 98% yield. In the case of demethylation of **10** with pyridinium chloride the bromine atom was partly removed to give a mixture of products.

For introduction of carbon-carbon double bonds into the seven-membered ring, compound **12** was acetylated with acetic anhydride and pyridine [20]. The acetylation reaction proceeded smoothly to afford 4-acetoxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one **13** in 95% yield. The ester **13** was brominated with bromine to give 4-acetoxy-6,6-dibromo-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one **14** in 66% yield [17,20,21]. When the bromide **14** was refluxed with lithium chloride in dimethylformamide, desired 4-hydroxy-5*H*-benzocyclohepten-5-one **15** was obtained in 74% yield [17,20,21]. The structure of **15** was determined by the nmr and ir spectra. The ^{1}H nmr spectrum of **15** showed complex peaks (m, 7H) due to protons on the benzene ring and seven-membered ring at 6.45-7.65 ppm and a peak (s, 1H) due to a strongly hydrogen-bonded hydroxyl group at 14.84 ppm. The ^{13}C nmr spectrum also supported the structure of **15**. The ir spectrum of **15** gave an absorption band of a carbonyl group at 1640 cm^{-1}. The reaction of **15** with ethyl bromoacetate in the presence of tripotassium phosphate followed by hydrolysis afforded (5-oxo-5*H*-benzocyclohepten-4-yloxy)acetic acid **16** in 97% yield. Thus, the starting material was obtained for the synthesis of cyclohepta[*cd*]-benzofuran **2**.

Two methods were attempted to synthesize compound **2**. Initially, when the acid **16** was heated at 150° for 1 hour with sodium acetate in acetic anhydride, the desired cyclohepta[*cd*]benzofuran **2** was obtained in 82% yield [1]. The structure of **2** was confirmed by ^{1}H and ^{13}C nmr spectra. The ^{1}H nmr spectrum exhibited peaks due to four protons on the seven-membered ring at 5.14-5.50 (m, 2H) and 5.76-6.04 ppm (m, 2H), showing olefinic character [4]. Protons on the benzene ring showed peaks at 6.35-6.45 (m, 1H) and 6.84-6.90 ppm (m, 2H). The proton on the furan ring appeared at 7.34 ppm (s, 1H). The ^{13}C nmr spectrum of **2** supported its structure. Secondly, cyclohepta[*cd*]-benzofuran **2** was synthesized in 60% yield by irradiation of the acid **16** in acetonitrile for 10 minutes [1,22]. The photoreaction proceeded very rapidly. The detail of the furan-ring formation by photocyclization is under study. Thus, the parent molecule of cyclohepta[*cd*]benzofuran was synthesized in good yield. Compound **2** is an orange crystalline solid prone to polymerize during storage in air, however, stable under reduced pressure in a desiccator at room temperature. Compound **2** is stable to heating.



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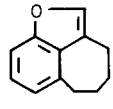

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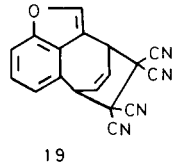

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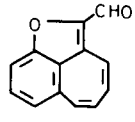

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Next, several reactions of cyclohepta[*cd*]benzofuran **2** were examined and compared with those of furan **1a**, heptafulvene, and benzofuran. The results are summarized in Formula 2. When trifluoroacetic acid was added to a deuteriochloroform solution of **2**, the solution turned deep purple. Its ^{1}H nmr spectrum exhibited a peak at 6.32 ppm (s, 2H) and complex peaks at 7.86-9.06 ppm (m, 7H), showing formation of a tropylium ion such as **17**. Protonation produced about 2.0-2.5 ppm shift to a lower magnetic field compared with chemical shifts of the parent molecule of **2**. By pouring the purple solution into water the starting

material **2** was recovered. Similarly, furan **1a** [1], heptafulvene [3,6], and benzoheptafulvene [4,5] produce a tropylium ion similar to **17** by protonation.

Catalytic hydrogenation of **2** with palladium on charcoal proceeded smoothly to give 3,4,5,6-tetrahydrocyclohepta[*cd*]benzofuran **18** in 93% yield. It shows that one carbon-carbon double bond in the furan ring is stabilized in the conjugated system of benzofuran [1]. In contrast, two carbon-carbon double bonds in the seven-membered ring have olefinic character as heptafulvene [3] and benzoheptafulvene [4].

When a benzene solution of furan **2** and tetracyanoethylene [6] was refluxed for 2 hours, the Diels-Alder reaction occurred to afford an adduct **19** in 31% yield [23]. Prolongation of the reaction time decreased the yield of **19** because the product is prone to decompose during the reaction. In the Diels-Alder reaction, two double bonds in the seven-membered ring of **1a** and **2** always react as diene [1,6]. In heptafulvene a similar reaction occurs but exo-double bonds are usually the reactive site [3,6].

Formylation of furan **2** with phosphorus oxychloride and dimethylformamide proceeded smoothly in 92% yield at room temperature to give compound **20**, showing high reactivity of the 2-position toward electrophilic reagents. Similarly, benzofuran is formylated at the 2-position [8]. Compound **20** is stable in air at room temperature owing to an electron-withdrawing formyl group. Finally, photocyclization [1,15,21] of furan **2** was attempted for 5 hours, however, such indenofuran as obtained by photocyclization of **1b** was not produced and the starting material was recovered.

Thus, reactivities of cyclohepta[*cd*]benzofuran **2** are very similar to those of compound **1a**. The results mentioned above suggest that cyclohepta[*cd*]benzofuran **2** has both properties of heptafulvene and benzofuran.

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. Polyphosphoric acid was prepared by heating a mixture of phosphorus pentoxide (525 g) and 85% phosphoric acid (670 g, 420 ml) at 140-150° for 5 hours. Photoreactions were carried out with 400-W high-pressure mercury lamp (Riko UVL-400HA) in a pyrex cylindrical vessel equipped with a nitrogen inlet. 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 on a JEOL JNM-FX 90Q FT nmr spectrometer, using tetramethylsilane as the internal standard.

3-(3-Methoxyphenyl)propenoic Acid (**4**).

A mixture of *m*-anisaldehyde **3** (50.0 g, 367 mmoles), malonic acid (80.0 g, 769 mmoles), piperidine (5.00 g, 58.8 mmoles), and pyridine (130 ml) was heated gradually up to 85° and kept at this temperature for 1 hour [9]. Then, the mixture was heated at 115° for 3 hours. The cooled solution was poured into ice-water and acidified with 6*M* hydrochloric acid (300 ml). The resulting precipitate was collected by filtration to give **4** (61.0 g, 98%); it formed colorless needles from aqueous methanol, mp 115-117° (lit [10], mp 118-120°); ir (potassium bromide): 1680 cm^{-1} (CO_2H); ^1H nmr (deuteriochloroform): δ 3.81 (s, 3H, OCH_3), 6.42 (d, J = 16 Hz, 1H, $CH=CHCO_2H$), 6.87-7.39 (m, 4H, Ar-H), 7.75 (d, J = 16 Hz, 1H, $CH=CHCO_2H$), 11.28 (broad s, 1H, CO_2H).

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66. Found: C, 67.40; H, 5.83.

3-(3-Methoxyphenyl)propionic Acid (**5**).

The acid **4** (50.0 g, 280 mmoles) dissolved in ethanol (160 ml) was hydrogenated for 1 hour at room temperature in the presence of 7% palladium on charcoal (2.00 g) as a catalyst. After removal of the catalyst by filtration the ethanol was evaporated. The resulting precipitate was washed with hexane to give **5** (44.5 g, 88%); it formed colorless plates from ether-hexane, mp 47-48° (lit [11], mp 44-45°); ir (potassium bromide): 1710 cm^{-1} (CO_2H); ^1H nmr (deuteriochloroform): δ 2.54-3.02 (m, 4H, CH_2CH_2), 3.76 (s, 3H, OCH_3), 6.73-6.80 (m, 3H, Ar-H), 7.10-7.20 (m, 1H, Ar-H), 10.78 (broad s, 1H, CO_2H); ^{13}C nmr (deuteriochloroform): δ 30.7 (t), 35.5 (t), 55.1 (q), 111.8 (d), 114.2 (d), 120.7 (d), 129.6 (d), 141.9 (s), 159.9 (s), 179.2 (s).

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.51; H, 6.75.

3-(3-Methoxyphenyl)propan-1-ol (**6**).

Lithium aluminum hydride (6.30 g, 166 mmoles) was added to dry tetrahydrofuran (140 ml) under cooling with ice-water. To the solution the acid **5** (30.0 g, 167 mmoles) in dry tetrahydrofuran (80.0 ml) was dropped during 1 hour with stirring [12]. The mixture was stirred for additional 2 hours at room temperature. The excess of lithium aluminum hydride was decomposed with 6*M* hydrochloric acid. The resulting product was extracted with ether. The extract was washed, dried, and evaporated to give **6** (27.6 g, 97%) as a colorless oil, bp 136° (4 Torr) (lit [24], bp 137-138° at 5.5 Torr); ir (neat): 3360 cm^{-1} (OH); ^1H nmr (deuteriochloroform): δ 1.68-2.00 (m, 2H, CH_2CH_2OH), 2.47 (s, 1H, OH), 2.65 (dd, J = 7 and 8 Hz, 2H, Ar-CH_2), 3.62 (t, J = 7 Hz, 2H, CH_2CH_2OH), 3.75 (s, 3H, OCH_3), 6.68-6.80 (m, 3H, Ar-H), 7.09-7.27 (m, 1H, Ar-H); ^{13}C nmr (deuteriochloroform): δ 32.1 (t), 34.1 (t), 55.0 (q), 61.8 (t), 111.1 (d), 114.3 (d), 120.9 (d), 129.3 (d), 143.6 (s), 159.7 (s).

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.98; H, 8.55.

1-(3-Bromopropyl)-3-methoxybenzene (**7**).

Phosphorus tribromide (26.5 g, 97.8 mmoles) in dry ether (20 ml) was added to the alcohol **6** (40.0 g, 241 mmoles) in dry ether (120 ml) under cooling with ice-water. The solution was refluxed for 1 hour [12] and poured into ice-water after cooling to decompose the excess of phosphorus tribromide. The resulting product was extracted with ether. The extract was washed with a 1*M* aqueous potassium carbonate solution, then with water, dried, and evaporated to give **7** (39.3 g, 71%) as a colorless oil, bp 120° (4 Torr); ^1H nmr (deuteriochloroform): δ 1.96-2.29 (m, 2H, CH_2CH_2Br), 2.74 (t, J = 7 Hz, 2H, Ar-CH_2), 3.37 (t, J = 7 Hz, 2H, CH_2CH_2Br), 3.77 (s, 3H, OCH_3), 6.64-6.81 (m, 3H, Ar-H), 7.10-7.28 (m, 1H, Ar-H); ^{13}C nmr (deuteriochloroform): δ 32.9 (t), 34.0 (t), 55.0 (q), 111.4 (d), 114.3 (d), 120.8 (d), 129.4 (d), 142.1 (s), 159.8 (s).

Anal. Calcd. for $C_{10}H_{13}BrO$: C, 52.40; H, 5.72. Found: C, 52.66; H, 5.58.

5-(3-Methoxyphenyl)pentanoic Acid (**8**).

Sixty percent sodium hydride (6.50 g, 271 mmoles) was added slowly to diethyl malonate (125 ml, 824 mmoles) in tetrahydrofuran (200 ml) under cooling with ice-water. To the above solution, **7** (50.0 g, 218 mmoles) in tetrahydrofuran (70 ml) was added dropwise during 15 minutes [12]. The mixture was refluxed for 3 hours. After cooling it was poured into ice-water and extracted with ether. The extract was washed, dried, and evaporated. The residue was dissolved in ethanol (120 ml) and hydrolyzed by refluxing for 1 hour with potassium hydroxide (150 g) in water (400 ml). The alkaline solution was washed with ether and acidified with 6*M* hydrochloric acid. The resulting oil was extracted with ether. The extract was washed, dried, and evaporated to give dicarboxylic acid as a colorless oil (54.1 g). The oil was heated at 190° for 40 minutes to give **8** (40.0 g, 88%) as a colorless oil, bp 192° (1.5 Torr) (lit [15], bp 142-143° at 0.17

Torr); ir (neat): 1710 cm^{-1} (CO_2H); ^1H nmr (deuteriochloroform): δ 1.55-1.71 (m, 4H, $CH_2CH_2CH_2CO_2H$), 2.24-2.40 (m, 2H, Ar-CH_2 or CH_2CO_2H), 2.51-2.64 (m, 2H, Ar-CH_2 or CH_2CO_2H), 3.73 (s, 3H, OCH_3), 6.66-6.70 (m, 3H, Ar-H), 7.07-7.25 (m, 1H, Ar-H), 10.32 (broad s, 1H, CO_2H); ^{13}C nmr (deuteriochloroform): δ 24.3 (t), 30.6 (t), 33.9 (t), 35.5 (t), 54.9 (q), 111.1 (d), 114.3 (d), 120.9 (d), 129.3 (d), 143.6 (s), 159.8 (s), 180.0 (s).

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 68.95; H, 7.88.

5-(2-Bromo-5-methoxyphenyl)pentanoic Acid (**9**).

Bromine (33.6 g, 210 mmoles) in chloroform (400 ml) was added to **8** (40.0 g, 192 mmoles) in chloroform (400 ml) during 1.5 hours under stirring and cooling with ice-water [16]. The solution was further stirred for 0.5 hour at room temperature and extracted with ether. The extract was washed, dried, and evaporated to give **9** (55.0 g, 99%); it formed colorless plates from ether-hexane, mp 44-46°; ir (potassium bromide): 1735, 1700 cm^{-1} (CO_2H); ^1H nmr (deuteriochloroform): δ 1.60-1.76 (m, 4H, $CH_2CH_2CH_2CO_2H$), 2.32-2.48 (m, 2H, Ar-CH_2 or CH_2CO_2H), 2.61-2.77 (m, 2H, Ar-CH_2 or CH_2CO_2H), 3.76 (s, 3H, OCH_3), 6.60 (dd, J = 3 and 9 Hz, 1H, Ar-H), 6.75 (d, J = 3 Hz, 1H, Ar-H), 7.38 (d, J = 9 Hz, 1H, Ar-H), 9.73 (broad s, 1H, CO_2H); ^{13}C nmr (deuteriochloroform): δ 24.3 (t), 29.2 (t), 33.9 (t), 35.9 (t), 55.3 (q), 113.1 (d), 114.9 (s), 116.1 (d), 133.2 (d), 142.2 (s), 159.0 (s), 180.0 (s).

Anal. Calcd. for $C_{12}H_{15}BrO_3$: C, 50.19; H, 5.27. Found: C, 50.09; H, 5.45.

1-Bromo-4-methoxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one (**10**).

A mixture of **9** (15.0 g, 52.3 mmoles) and polyphosphoric acid (1200 g) was heated at 55° for 8 hours with stirring [17,18]. The mixture was poured into ice-water and extracted three times with benzene. The combined extract was washed with an aqueous potassium carbonate solution, then with water, dried, and evaporated to give **10** (8.50 g, 60%); it formed colorless needles from methanol, mp 78-79°; ir (potassium bromide): 1690 cm^{-1} (CO); ^1H nmr (deuteriochloroform): δ 1.68-1.80 (m, 4H, $CH_2CH_2CH_2CO$), 2.52-2.66 (m, 2H, Ar-CH_2 or CH_2CO), 2.82-2.98 (m, 2H, Ar-CH_2 or CH_2CO), 3.78 (s, 3H, OCH_3), 6.72 (d, J = 9 Hz, 1H, C_2-H or C_3-H), 7.51 (d, J = 9 Hz, 1H, C_2-H or C_3-H); ^{13}C nmr (deuteriochloroform): δ 22.2 (t), 23.7 (t), 30.9 (t), 41.7 (t), 56.1 (q), 118.8 (d), 114.3 (s), 130.9 (s), 134.6 (d), 137.6 (s), 155.1 (s), 205.7 (s).

Anal. Calcd. for $C_{12}H_{13}BrO_2$: C, 53.55; H, 4.87. Found: C, 53.34; H, 4.98.

4-Methoxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one (**11**).

The bromide **10** (20.0 g, 74.3 mmoles) dissolved in ethanol (150 ml) was hydrogenated for 3.5 hours at room temperature in the presence of 7% palladium on charcoal (1.00 g) and triethylamine (20.0 g, 198 mmoles) [16]. After removal of the catalyst by filtration the ethanol was evaporated. The residue was extracted with ether. The extract was washed twice with 2*M* hydrochloric acid, then with water, dried, and evaporated to give **11** (13.7 g, 96%); it formed colorless plates from methanol, mp 84-85°; ir (potassium bromide): 1680 cm^{-1} (CO); ^1H nmr (deuteriochloroform): δ 1.71-1.85 (m, 4H, $CH_2CH_2CH_2CO$), 2.54-2.78 (m, 4H, Ar-CH_2 and CH_2CO), 3.77 (s, 3H, OCH_3), 6.70 (d, J = 8 Hz, 1H, C_1-H or C_3-H), 6.80 (d, J = 8 Hz, 1H, C_1-H or C_3-H), 7.24 (t, J = 8 Hz, 1H, C_2-H); ^{13}C nmr (deuteriochloroform): δ 23.4 (t), 25.8 (t), 32.7 (t), 42.5 (t), 55.9 (q), 109.9 (d), 121.0 (d), 129.9 (s), 131.0 (d), 139.3 (s), 156.0 (s), 207.0 (s).

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.74; H, 7.43.

4-Hydroxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one (**12**).

A mixture of **11** (18.0 g, 94.7 mmoles) and pyridinium chloride (90.0 g, 779 mmoles) was heated at 200° for 1 hour [19]. The mixture was poured into ice-water and extracted with ether. The extract was washed with 2*M* hydrochloric acid, then with water, dried, and evaporated to give **12** (16.4 g, 98%) as a yellow oil, bp 138° (3 Torr); ir (neat): 1630 cm^{-1} (CO); ^1H nmr (deuteriochloroform): δ 1.77-1.95 (m, 4H, $CH_2CH_2CH_2CO$), 2.75-3.01 (m, 4H, Ar-CH_2 and CH_2CO), 6.70 (d, J = 9 Hz, 1H, C_1-H or C_3-H), 6.80 (d, J = 9 Hz, 1H, C_1-H or C_3-H), 7.28 (t, J = 9 Hz, 1H, C_2-H), 12.41 (s, 1H, OH); ^{13}C nmr (deuteriochloroform): δ 20.5 (t), 24.8 (t), 33.3 (t), 41.7 (t), 116.3 (d), 120.4 (s), 121.0 (d), 135.0 (d), 145.2 (s), 163.2 (s), 209.6 (s).

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.70; H, 6.97.

4-Acetoxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one (**13**).

A mixture of **12** (20.0 g, 114 mmoles), acetic anhydride (20 ml, 211 mmoles), and pyridine (80 ml) was stirred for 5 hours at room temperature [20]. The mixture was poured into ice-water, stirred for 15 minutes to decompose the excess of acetic anhydride, and extracted with ether. The extract was washed twice with 2*M* hydrochloric acid, then with water, dried, and evaporated to give **13** (23.7 g, 95%); it formed colorless plates from hexane, mp 64-65°; ir (potassium bromide): 1755 (CH_3CO_2), 1690 cm^{-1} (CO); ^1H nmr (deuteriochloroform): δ 1.74-1.88 (m, 4H, CH_2CH_2CO), 2.23 (s, 3H, $COCH_3$), 2.50-2.68 (m, 2H, Ar-CH_2 or CH_2CO), 2.74-2.88 (m, 2H, Ar-CH_2 or CH_2CO), 6.94 (dd, J = 1 and 8 Hz, 1H, C_1-H or C_3-H), 7.03 (dd, J = 1 and 8 Hz, 1H, C_1-H or C_3-H), 7.35 (t, J = 8 Hz, 1H, C_2-H); ^{13}C nmr (deuteriochloroform): δ 20.9 (q), 21.5 (t), 25.4 (t), 32.1 (t), 41.1 (t), 120.8 (d), 126.5 (d), 131.3 (d), 132.6 (s), 140.0 (s), 147.4 (s), 169.5 (s), 205.7 (s).

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.65; H, 6.67.

4-Acetoxy-6,6-dibromo-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one (**14**).

Bromine (16.0 g, 100 mmoles) in carbon tetrachloride (30 ml) was added during 2.5 hours with stirring at room temperature to **13** (10.0 g, 45.9 mmoles) in carbon tetrachloride (120 ml) [17,20,21]. The solution was further stirred for 0.5 hour and extracted with ether. The extract was washed, dried, and evaporated. The resulting crystals were washed with cold methanol to give **14** (11.4 g, 66%); it formed colorless plates from methanol, mp 82-83°; ir (potassium bromide): 1770 (CH_3CO_2), 1705 cm^{-1} (CO); ^1H nmr (deuteriochloroform): δ 1.84-2.11 (m, 2H, $CH_2CH_2CH_2$), 2.26 (s, 3H, CH_3CO_2), 2.74 (t, J = 6 Hz, 4H, $CH_2CH_2CH_2$), 7.05 (dd, J = 1 and 7 Hz, 1H, C_1-H or C_3-H), 7.10 (dd, J = 1 and 8 Hz, 1H, C_1-H or C_3-H), 7.44 (dd, J = 7 and 8 Hz, 1H, C_2-H); ^{13}C nmr (deuteriochloroform): δ 20.6 (q), 25.0 (t), 30.3 (t), 44.7 (t), 69.2 (s), 121.8 (d), 125.9 (s), 128.4 (d), 132.0 (d), 138.0 (s), 147.8 (s), 168.7 (s), 191.4 (s).

Anal. Calcd. for $C_{13}H_{12}Br_2O_3$: C, 41.52; H, 3.22. Found: C, 41.60; H, 3.48.

4-Hydroxy-5*H*-benzocyclohepten-5-one (**15**).

A mixture of **14** (10.0 g, 266 mmoles), lithium chloride (4.00 g, 94.3 mmoles), and dimethylformamide (170 ml) was refluxed for 3 hours under nitrogen atmosphere [17,20,21]. The mixture was poured into ice-water and extracted with ether. The extract was washed, dried, and evaporated. The residue was chromatographed and eluted with benzene to give **15** (3.40 g, 74%); it formed orange plates from methanol, mp 97-98°; ir (potassium bromide): 1640 cm^{-1} (CO); ^1H nmr (deuteriochloroform): δ 6.45-7.65 (m, 7H, C_1-H, C_2-H, C_3-H, C_6-H, C_7-H, C_8-H, and C_9-H), 14.84 (s, 1H, OH); ^{13}C nmr (deuteriochloroform): δ 119.4 (d), 122.8 (s), 125.2 (d), 126.1 (d), 134.4 (d), 136.3 (d), 137.5 (d), 138.0 (s), 142.0 (d), 165.2 (s), 193.4 (s).

Anal. Calcd. for $C_{11}H_8O_2$: C, 76.73; H, 4.68. Found: C, 76.67; H, 4.89.

(5-Oxo-5*H*-benzocyclohepten-4-yloxy)acetic Acid (**16**).

A mixture of **15** (2.00 g, 11.6 mmoles), ethyl bromoacetate (4.00 g, 23.9 mmoles), tripotassium phosphate (5.20 g, 24.5 mmoles), and dimethylsulfoxide (30.0 ml) was stirred at 60° for 0.5 hour [1]. The mixture was poured into ice-water and extracted with ether. The extract was washed, dried, and evaporated. The residue was dissolved in ethanol (20.0 ml) and hydrolyzed by adding a 2*M* aqueous potassium hydroxide solution. The alkaline solution was acidified with 6*M* hydrochloric acid and the resulting precipitate was extracted with ether. The extract was washed, dried, and evaporated to give **16** (2.60 g, 97%); it formed colorless prisms from acetone, mp 138-139°; ir (potassium bromide): 1745 (CO_2H), 1640 cm^{-1} (CO); ^1H nmr (deuterioacetone): δ 4.94 (s, 2H, OCH_2), 6.72-7.81 (m, 7H, C_1-H, C_2-H, C_3-H, C_6-H, C_7-H, C_8-H, and C_9-H).

Anal. Calcd. for $C_{13}H_{10}O_4$: C, 67.82; H, 4.38. Found: C, 67.52; H, 4.47.

Cyclohepta[*cd*]benzofuran (**2**).

A mixture of **16** (1.70 g, 7.39 mmoles), sodium acetate (7.80 g, 95.1 mmoles), and acetic anhydride (25.0 ml) was heated at 150° for 1 hour [1]. The mixture was poured into ice-water, stirred for 15 minutes to decompose the excess of acetic anhydride. The resulting precipitate was extracted with ether. The extract was washed with a 1*M* aqueous potassium carbonate solution, then with water, dried, and evaporated. The residue was chromatographed and eluted with benzene(1)-hexane(1) to give **2** (1.02 g, 82%); it formed orange plates from aqueous methanol, mp 58-59°; ^{1}H nmr (deuteriochloroform): δ 5.14-5.50 (m, 2H, C_3-H, C_4-H, C_5-H, or C_6-H), 5.76-6.04 (m, 2H, C_3-H, C_4-H, C_5-H, or C_6-H), 6.35-6.45 (m, 1H, C_7-H, C_8-H, or C_9-H), 6.84-6.90 (m, 2H, C_7-H, C_8-H, or C_9-H), 7.34 (s, 1H, C_2-H); ^{13}C nmr (deuteriochloroform): δ 111.5 (d), 121.2 (d), 124.4 (s), 125.3 (d), 125.9 (d), 126.3 (d), 127.6 (d), 130.5 (s), 133.5 (d), 135.5 (s), 137.7 (d), 156.6 (s).

Anal. Calcd. for $C_{12}H_8O$: C, 85.69; H, 4.79. Found: C, 85.52; H, 4.91.

Synthesis of Cyclohepta[*cd*]benzofuran **2** by Photocyclization.

An acetonitrile solution (500 ml) of **16** (0.460 g, 2.00 mmoles) was deoxygenated by bubbling nitrogen gas for 1 hour and irradiated for 10 minutes at room temperature [1,22]. After removal of the acetonitrile the residue was chromatographed and eluted with benzene(1)-hexane(1) to give **2** (0.201 g, 60%).

Protonation of **2** with Trifluoroacetic Acid.

Furan **2** (30 mg, 0.178 mmole) was dissolved in deuteriochloroform (0.37 ml) in the nmr tube. To the above solution trifluoroacetic acid (0.14 ml) was added [1,3-6]. The solution immediately turned deep purple. The nmr spectrum of the solution was determined at room temperature, showing the formation of the tropylium ion **17**; ^{1}H nmr (deuteriochloroform): δ 6.32 (s, 2H, C_2-H_2), 7.86-9.06 (m, 7H, C_3-H, C_4-H, C_5-H, C_6-H, C_7-H, C_8-H, and C_9-H).

Catalytic Hydrogenation of **2** with Palladium on Charcoal.

Furan **2** (0.200 g, 1.19 mmoles) in ethanol (20.0 ml) was hydrogenated for 1.5 hours in the presence of 7% palladium on charcoal [1,3,4]. After removal of the catalyst by filtration the ethanol was evaporated. The residue was chromatographed and eluted with benzene(1)-hexane(9) to give 3,4,5,6-tetrahydrocyclohepta[*cd*]benzofuran (**18**, 0.190 g, 93%) as a colorless oil, bp 112° (2 Torr); ^{1}H nmr (deuteriochloroform): δ 1.90-2.00 (m, 4H, C_4-H_2 and C_5-H_2), 2.72-2.85 (m, 2H, C_3-H_2 or C_6-H_2), 3.06-3.12 (m, 2H, C_3-H_2 or C_6-H_2), 6.89-7.32 (m, 4H, C_2-H, C_7-H, C_8-H, and C_9-H); ^{13}C nmr (deuteriochloroform): δ 26.0 (t), 28.3 (t), 28.8 (t), 36.4 (t), 108.5 (d), 120.7 (s), 122.1 (d), 123.7 (d), 127.2 (s), 136.8 (s), 140.1 (d), 156.0 (s).

Anal. Calcd. for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.69; H, 7.17.

Reaction of **2** with Tetracyanoethylene.

A mixture of **2** (0.200 g, 1.19 mmoles), tetracyanoethylene (0.168 g, 1.31 mmoles), and benzene (10.0 ml) was refluxed for 2 hours [1,6]. Prolongation of the reaction time decreased yield of the product because of decomposition. The benzene solution was chromatographed and eluted with benzene(97)-ether(3) to give **19** (0.110 g, 31%); it formed colorless plates from aqueous acetone, mp 180-182° dec; ir (potassium bromide): 2240 cm^{-1} (CN); ^{1}H nmr (deuteriochloroform): δ 5.01-5.20 (m, 2H, C*H*CH=CHC*H*), 6.74-7.06 (m, 2H, CHC*H*=C*H*CH), 7.35-7.67 (m, 3H, Ar-H), 8.13 (s, 1H, Furan-H).

Anal. Calcd. for $C_{18}H_8N_4O$: C, 72.97; H, 2.72; N, 18.91. Found: C, 72.75; H, 3.01; N, 18.71.

Formylation of **2** with Phosphorus Oxychloride and Dimethylformamide.

Phosphorus oxychloride (1.20 g, 7.84 mmoles) in dimethylformamide (3.0 ml) was added to **2** (0.400 g, 2.04 mmoles) in dimethylformamide (25 ml) and the solution was stirred for 3 hours at room temperature [1,8]. The solution was poured into ice-water and stood for 2 days to precipitate the product. The resulting precipitate was extracted with ether. The extract was washed, dried, and evaporated. The residue was chromatographed and eluted with benzene(95)-ether(5) to give **20** (0.430 g, 92%); it formed red needles from benzene-hexane, mp 106-107°; ir (potassium bromide): 1650 cm^{-1} (CO); ^{1}H nmr (deuteriochloroform): δ 5.71-6.05 (m, 2H, C_3-H, C_4-H, C_5-H, or C_6-H), 6.22-6.42 (m, 1H, C_3-H, C_4-H, C_5-H, or C_6-H), 6.65-6.72 (m, 1H, C_3-H, C_4-H, C_5-H, or C_6-H), 6.80-7.38 (m, 3H, C_7-H, C_8-H, and C_9-H), 9.76 (s, 1H, CHO); ^{13}C nmr (deuteriochloroform): δ 111.5 (d), 121.9 (d), 124.6 (d), 128.5 (d), 130.3 (s), 130.5 (d), 131.9 (d), 132.7 (s), 136.1 (d), 137.1 (s), 143.9 (s), 156.6 (s), 177.7 (d).

Anal. Calcd. for $C_{13}H_8O_2$: C, 79.58; H, 4.11. Found: C, 79.36; H, 4.30.

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