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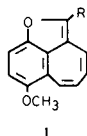
Received May 20, 1987

Cyclohepta[*cd*]benzofurans **1a-c** were synthesized by heating (5-oxo-5*H*-benzocyclohepten-4-yloxy)acetic acids **7a-c** with sodium acetate in acetic anhydride or by irradiation of **7a-c** in acetonitrile. Several reactions such as protonation, catalytic hydrogenation, Diels-Alder reaction, acylation, and photoreaction were examined for **1a-b**. The results show that cyclohepta[*cd*]benzofurans have both properties of heptafulvene and benzofuran. The carbon-carbon double bond in the furan ring of **1a** has aromatic character, however, the carbon-carbon double bonds in the seven-membered ring have olefinic character.

J. Heterocyclic Chem., **25**, 39 (1988).

Introduction.

Nonbenzenoid aromatic compounds have been investigated for a long time. Tropone [2], heptafulvene [3,4], and benzoheptafulvene [5,6] are interesting substances in non-benzenoid aromatic compounds. It seems that the double bonds in heptafulvene have olefinic character rather than aromatic character [7]. However, when electron-withdrawing groups such as a cyano or carbonyl group are substituted in heptafulvene the double bonds become much stable, because the seven-membered ring has a positive charge [8]. On the other hand, electron-donating groups such as an oxygen or nitrogen atom will destabilize the conjugated system of heptafulvene as the seven-membered ring has a negative charge [9]. In the previous paper [10], we reported briefly synthesis of cyclohepta[*cd*]benzofuran **1a**. The compound **1a** has both structures of heptafulvene and benzofuran in the molecule. Therefore, the properties of cyclohepta[*cd*]benzofuran are very interesting. In the present paper we synthesize cyclohepta[*cd*]benzofuran derivatives and examine their chemical properties to compare with those of heptafulvene and benzofuran.



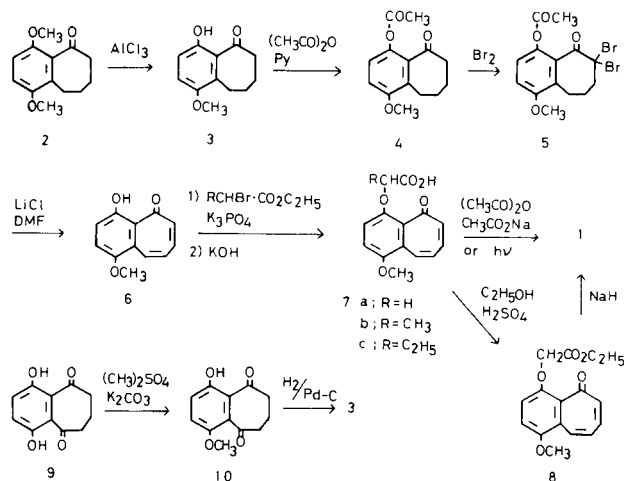
- a ; R = H
b ; R = CH₃
c ; R = C₂H₅
d ; R = CO₂H
e ; R = CHO
f ; R = COCH₃

Formula 1

Results and Discussion.

Initially, synthesis of cyclohepta[*cd*]benzofurans **1a-c** was examined. The synthetic methods of **1a-c** are summarized in Scheme 1. For synthesis of **1a-c** 1,4-dimethoxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one (**2**) [11] was employed as the starting material. When compound **2** was

treated with aluminum chloride in nitrobenzene only one methyl group was removed to give hydroxyketone **3** in 80% yield [12]. Compound **3** was readily acetylated to acetate **4** in 98% yield using acetic anhydride and pyridine [13]. To introduce double bonds into the seven-membered ring the acetate **4** was brominated with bromine to give dibromide **5** in 75% yield [13-15]. By heating the dibromide **5** with lithium chloride in dimethylformamide the desired 4-hydroxybenzocyclohepten-5-one **6** was obtained in 56% yield [13,15]. When compound **6** was heated with ethyl bromoacetate in dimethyl sulfoxide in the presence of tripotassium phosphate followed by saponification, carboxylic acid **7a** was prepared in 93% yield [10]. Similarly, the reactions of **6** and ethyl 2-bromopropionate or ethyl 2-bromobutyrate afforded the corresponding carboxylic acids **1b** (86%) or **1c** (88%) respectively. Dimethyl sulfoxide is a more satisfactory solvent than acetone or dioxane for ether synthesis from hydrogen-bonded hydroxy compounds [10]. By heating **7a** with

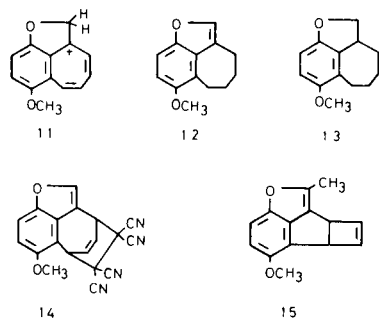


Scheme 1

sodium acetate in acetic anhydride cyclohepta[*cd*]benzofuran **1a** was obtained in 92% yield. Similar reactions of **7b** and **7c** afforded the corresponding cyclohepta[*cd*]benzofurans **1b** and **1c** in 90 and 91% yields respectively. The structures of **1a-c** were confirmed by the ^1H and ^{13}C nmr spectra. Compound **1a** is a red oil prone to polymerize during storage in air, but stable under reduced pressure. Compounds **1b** and **1c** are red crystalline solids and are much more stable in air than **1a**.

Furthermore, cyclohepta[*cd*]benzofurans **1a-c** were synthesized by a photocyclization reaction [16]. Irradiation of the acid **7a** in acetonitrile gave the furan **1a** in 14% yield. Similar photocyclizations of the acids **7b** and **7c** produced the corresponding furans **1b** and **1c** in 50 and 67% yields respectively, indicating a useful method for furan ring formation. Next, we examined the preparation of cyclohepta[*cd*]benzofurans using strong bases. The carboxylic acid **7a** was ethylated by refluxing in ethanol in the presence of sulfuric acid to give an ester **8** in 84% yield. When the ester **8** was heated with sodium hydride in dioxane the furan **1a** and furan-2-carboxylic acid **1d** were obtained in 53 and 34% yields respectively. However, potassium hydroxide failed to give **1a** and **1d** because of decomposition to tar-like products. The carboxylic acid **1d** is very stable and does not polymerize during storage in air.

As mentioned above cyclohepta[*cd*]benzofurans **1** were synthesized through five steps starting from 4-hydroxybenzocyclohepten-5-one **3**. During this study we found a facile synthetic method for compound **3**. When hydroquinone and glutaric acid was heated with aluminum chloride, 1,4-dihydroxybenzocycloheptene-5,9-dione **9** [17] was obtained in 50% yield. One of two hydroxyl groups in **9** was methylated with dimethylsulfate and potassium carbonate to give **10** in 52% yield. Though the yields of two of the steps were not so good, the reaction procedure was very easy. When the compound **10** was subjected to catalytic hydrogenation one carbonyl group which was not hydrogen-bonded was reduced selectively to afford **3** in 93% yield. This synthetic method is favorable for the preparation of compound **3** in a short time.



Formula 2

Secondly, several reactions of **1a** were examined and compared with those of heptafulvene and benzofuran. The results are summarized in Formula 2. When trifluoroacetic acid was added to a deuteriochloroform solution of **1a** the solution turned deep green. Its ^1H nmr spectrum suggested production of cation **11** from the following absorptions. The spectrum of **11** showed a peak (s, 2H) at 6.27 ppm due to the methylene protons in the furan ring and four olefinic protons in the seven-membered ring at a much lower magnetic field (7.98-9.53 ppm) compared with those (5.10-6.38 ppm) of the parent molecule of **1a**. The formation of a tropylium ion suggests that the conjugated system of **1a** is similar to the character of heptafulvene [4-6,18]. By adding water to the solution of **11** the starting material **1a** was recovered unchanged. Catalytic hydrogenation of **1a** with palladium on charcoal proceeded smoothly to give a tetrahydro-derivative **12** in 93% yield. However, reduction of the carbon-carbon double bond in the furan ring was difficult. The results show that the two double bonds in the seven-membered ring of **1a** are as easily subject to reduction as those in heptafulvene [4,5], but the double bond in the furan ring has aromatic character similar to that in benzofuran. Furthermore, when compound **1a** was reduced with sodium-ethanol the tetrahydro-derivative **12** and a hexahydro-derivative **13** were obtained in 20 and 68% yields respectively. It seems that compound **13** was derived from **12** since **12** was reduced to **13** under the same conditions. The Diels-Alder reaction was examined between **1a** and some olefines. When **1a** was refluxed with tetracyanoethylene [15,16] in benzene an adduct **14** was obtained in 88% yield. However, **1a** did not react with diethyl acetylenedicarboxylate [4,19] or with benzoquinone [20]. In heptafulvene a similar Diels-Alder reaction occurs but *exo*-double bonds are usually the reactive site [4,15,16]. Next, reactions on the furan ring of **1a** was examined. Compound **1a** was readily formylated with phosphorus oxychloride and dimethylformamide to give **1e** in 97% yield. By acetylation of **1a** with acetyl chloride and stannic chloride **1f** was obtained in 16%. The results of formylation [21] and acetylation [22] of **1a** are similar to those of benzofuran. Compounds **1e** and **1f** are stable in air owing to an electron-withdrawing effect of the formyl or the acetyl group. Bromination of **1a** with bromine or *N*-bromosuccinimide afforded a complex mixture. Photoreaction of cyclohepta[*cd*]benzofuran **1b** was examined because **1a** was less reactive. Irradiation of **1b** in acetonitrile for 2 hours gave an indenofuran derivative **15** in 25% yield. It seems that compound **15** has considerable strain in the molecule because the ir and ^{13}C nmr spectra show peaks due to a carbon-carbon double bond at abnormal positions (see Experimental). To our knowledge literature on photocyclization of heptafulvene are not found, however, similar cyclization occurs for benzotropone [14].

Judging from the reactions of **1a** and **1b** mentioned above, it appears that cyclohepta[*cd*]benzofuran has both properties of a heptafulvene and a benzofuran. Especially, the carbon-carbon double bond in the furan ring has aromatic character and the carbon-carbon double bonds in the seven-membered ring has olefinic character.

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. 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 EPI-G grating ir spectrophotometer. The nmr spectra (^1H and ^{13}C nmr) were determined at 90 MHz on a JEOL JNM-FX 90Q FT NMR spectrometer, using tetramethylsilane as the internal standard.

4-Hydroxy-1-methoxy-6,7,8,9-tetrahydro-5H-benzocyclohepten-5-one (3).

Anhydrous aluminum chloride (14.0 g, 105 mmoles) in nitrobenzene (200 ml) was added to **2** [11] (20.0 g, 90.9 mmoles) in nitrobenzene (100 ml) and the mixture was heated at 75° for 6 hours with stirring. The mixture was decomposed with hydrochloric acid-ice and extracted with ether. The extract was washed, dried, and evaporated. After removal of the nitrobenzene under reduced pressure the product was distilled to give **3** (15.4 g, 82%), bp 126-131° (0.7 Torr); it formed yellow needles from methanol, mp 29-30°; ir (potassium bromide): 1630 cm^{-1} (CO); ^1H nmr (deuteriochloroform): δ 1.73-1.87 (m, 4H, $\text{C}_7\text{-H}_2$ and $\text{C}_8\text{-H}_2$), 2.74-2.87 (m, 2H, $\text{C}_9\text{-H}_2$), 2.93-3.07 (m, 2H, $\text{C}_6\text{-H}_2$), 3.78 (s, 3H, OCH_3), 6.79 (d, $J = 9$ Hz, 1H, $\text{C}_2\text{-H}$ or $\text{C}_3\text{-H}$), 7.06 (d, $J = 9$ Hz, 1H, $\text{C}_2\text{-H}$ or $\text{C}_3\text{-H}$), 11.56 (s, 1H); ^{13}C nmr (deuteriochloroform): δ 21.0 (t), 23.5 (t), 24.4 (t), 41.8 (t), 57.2 (q), 115.8 (d), 120.2 (d), 121.6 (s), 132.6 (s), 149.6 (s), 156.1 (s), 209.9 (s).

Anal. Calcd. for $\text{C}_{12}\text{H}_{14}\text{O}_3$: C, 69.88; H, 6.84. Found: C, 69.94; H, 6.90.

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

A mixture of **3** (30.0 g, 146 mmoles), acetic anhydride (30 ml), and pyridine (120 ml) was stirred at room temperature for 5 hours [13]. The mixture was poured into ice-water and extracted with ether. The extract was washed with 2M hydrochloric acid (100 ml x 3) then with water, dried, and evaporated to give **4** (35.4 g, 98%); it formed colorless needles from hexane, mp 71.5-73°; ir (potassium bromide): 1760 (CO_2), 1690 cm^{-1} (CO); ^1H nmr (deuteriochloroform): δ 1.68-1.82 (m, 4H, $\text{C}_7\text{-H}_2$ and $\text{C}_8\text{-H}_2$), 2.21 (s, 3H, CH_3CO_2), 2.50-2.64 (m, 2H, $\text{C}_9\text{-H}_2$), 2.76-2.90 (m, 2H, $\text{C}_6\text{-H}_2$), 3.81 (s, 3H, OCH_3), 6.90 (s, 2H, $\text{C}_2\text{-H}$ and $\text{C}_3\text{-H}$); ^{13}C nmr (deuteriochloroform): δ 20.8 (q), 21.5 (t), 23.1 (t), 24.2 (t), 41.0 (t), 56.1 (q), 113.2 (d), 120.9 (d), 128.0 (s), 133.7 (s), 140.3 (s), 154.0 (s), 170.0 (s), 205.8 (s).

Anal. Calcd. for $\text{C}_{14}\text{H}_{16}\text{O}_4$: C, 67.73; H, 6.50. Found: C, 67.65; H, 6.69.

4-Acetoxy-6,6-dibromo-1-methoxy-6,7,8,9-tetrahydro-5H-benzocyclohepten-5-one (5).

Bromine (27.0 g, 169 mmoles) in carbon tetrachloride (50 ml) was added to **4** (20.0 g, 80.6 mmoles) in carbon tetrachloride (220 ml) during 3 hours at room temperature [13-15]. The mixture was extracted with ether. The extract was washed, dried, and evaporated to give **5**; it formed yellow needles (25.0 g, 76%) from methanol, mp 98-99°; ir (potassium bromide): 1770 (CO_2), 1720 cm^{-1} (CO); ^1H nmr (deuteriochloroform): δ 1.76-2.05 (m, 2H, $\text{C}_9\text{-H}_2$), 2.25 (s, 3H, CH_3CO_2), 2.65-2.84 (m, 4H, $\text{C}_7\text{-H}_2$ and $\text{C}_8\text{-H}_2$), 3.83 (s, 3H, OCH_3), 6.97 (d, $J = 9$ Hz, 1H, $\text{C}_2\text{-H}$ or $\text{C}_3\text{-H}$), 7.08 (d, $J = 9$ Hz, 1H, $\text{C}_2\text{-H}$ or $\text{C}_3\text{-H}$); ^{13}C nmr (deuteriochloroform): δ 20.7 (q), 22.1 (t), 24.0 (t), 44.7 (t), 56.1 (q), 69.0 (s), 114.0 (d), 122.2 (d), 125.8 (s), 129.5 (s), 140.6 (s), 153.7 (s), 169.4 (s), 191.3 (s).

Anal. Calcd. for $\text{C}_{14}\text{H}_{14}\text{Br}_2\text{O}_4$: C, 41.41; H, 3.47. Found: C, 41.68; H, 3.65.

4-Hydroxy-1-methoxy-5H-benzocyclohepten-5-one (6).

A mixture of **5** (18.0 g, 44.1 mmoles), lithium chloride (7.0 g, 165 mmoles), and dimethylformamide (300 ml) was refluxed for 4 hours under a nitrogen atmosphere [13,15]. After removal of the dimethylformamide by distillation the residue was poured into ice-water and extracted with benzene. The extract was washed, dried, and evaporated. The residue was chromatographed and eluted with benzene to give **6** (5.0 g, 56%); it formed red needles from methanol, mp 88-89°; ir (potassium bromide): 1630 cm^{-1} (CO); ^1H nmr (deuteriochloroform): δ 3.90 (s, 3H, OCH_3), 6.51-7.33 (m, 3H, $\text{C}_7\text{-H}$, $\text{C}_8\text{-H}$, and $\text{C}_9\text{-H}$), 7.13 (d, $J = 9$ Hz, 1H, $\text{C}_2\text{-H}$ or $\text{C}_3\text{-H}$), 7.28 (d, $J = 9$ Hz, 1H, $\text{C}_2\text{-H}$ or $\text{C}_3\text{-H}$), 8.08 (d, $J = 12$ Hz, $\text{C}_5\text{-H}$), 14.13 (OH); ^{13}C nmr (deuteriochloroform): δ 57.4 (q), 118.6 (d), 120.0 (d), 123.8 (s), 125.6 (d), 126.9 (s), 133.2 (d), 135.9 (d), 137.9 (d), 150.8 (s), 158.2 (s), 193.9 (s).

Anal. Calcd. for $\text{C}_{12}\text{H}_{10}\text{O}_3$: C, 71.28; H, 4.98. Found: C, 70.99; H, 5.08.

(1-Methoxy-5-oxo-5H-benzocyclohepten-4-yloxy)acetic Acid (7a).

A mixture of **6** (4.0 g, 19.8 mmoles), ethyl bromoacetate (8.0 g, 47.9 mmoles), tripotassium phosphate (10.4 g, 49.1 mmoles), and dimethyl sulfoxide (50 ml) was heated at 60° for 40 minutes with stirring [10]. The mixture was poured into ice-water and extracted with ether. The extract was washed, dried, and evaporated. The residue was dissolved in ethanol (30 ml) and saponified with a 2M aqueous potassium hydroxide solution. The alkaline solution was acidified with 6M hydrochloric acid and the resulting precipitate was extracted with ether. The extract was washed, dried and evaporated to give **7a** (4.8 g, 93%); it formed yellow prisms from acetone, mp 150-151°; ir (potassium bromide): 1770 (CO_2H), 1640 cm^{-1} (CO); ^1H nmr (deuteriochloroform): δ 3.95 (s, 3H, OCH_3), 4.85 (s, 2H, OCH_2), 6.64-7.28 (m, 5H, $\text{C}_2\text{-H}$, $\text{C}_3\text{-H}$, $\text{C}_7\text{-H}$, $\text{C}_8\text{-H}$, and $\text{C}_9\text{-H}$), 7.99 (d, $J = 12$ Hz, 1H, $\text{C}_6\text{-H}$); ^{13}C nmr (deuteriochloroform): δ 56.7 (q), 68.7 (t), 113.2 (d), 116.7 (d), 126.7 (s), 127.1 (d), 129.8 (s), 129.9 (d), 134.1 (d), 134.9 (d), 149.3 (s), 152.7 (s), 170.2 (s), 191.5 (s).

Anal. Calcd. for $\text{C}_{14}\text{H}_{12}\text{O}_5$: C, 64.61; H, 4.65. Found: C, 64.39; H, 4.68.

2-(1-Methoxy-5-oxo-5H-benzocyclohepten-4-yloxy)propionic Acid (7b).

Compound **7b** (86%) was prepared from the reaction of **6** with ethyl 2-bromopropionate in a manner similar to the synthesis of **7a**; it formed yellow needles from acetone, mp 142-143°; ir (potassium bromide): 1755 (CO_2H), 1640 cm^{-1} (CO); ^1H nmr (deuteriochloroform): δ 1.72 (d, $J = 7$ Hz, 3H, CH_3CH), 3.91 (s, 3H, OCH_3), 5.05 (q, $J = 7$ Hz, 1H, CH_2CH), 6.65-7.32 (m, 5H, $\text{C}_2\text{-H}$, $\text{C}_3\text{-H}$, $\text{C}_7\text{-H}$, $\text{C}_8\text{-H}$, and $\text{C}_9\text{-H}$), 7.89-8.03 (m, 1H, $\text{C}_6\text{-H}$).

Anal. Calcd. for $\text{C}_{15}\text{H}_{14}\text{O}_5$: C, 65.69; H, 5.15. Found: C, 65.47; H, 5.12.

2-(1-Methoxy-5-oxo-5H-benzocyclohepten-4-yloxy)butyric Acid (7c).

Compound **7c** (88%) was prepared from the reaction of **6** with ethyl 2-bromobutyrate in a manner similar to the synthesis of **7a**; it formed yellow plates from methanol, mp 118-119°; ir (potassium bromide): 1740 (CO_2H), 1640 cm^{-1} (CO); ^1H nmr (deuteriochloroform): δ 1.12 (t, $J = 7$ Hz, 3H, CH_2CH_2), 2.08 (dt, $J = 6$ and 6 Hz, 2H, CH_2CH_2), 3.91 (s, 3H, OCH_3), 4.98 (t, $J = 6$ Hz, 1H, CHCO_2), 6.67-7.33 (m, 5H, $\text{C}_2\text{-H}$, $\text{C}_3\text{-H}$, $\text{C}_7\text{-H}$, $\text{C}_8\text{-H}$, and $\text{C}_9\text{-H}$), 7.89-8.02 (m, 1H, $\text{C}_6\text{-H}$).

Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_5$: C, 66.66; H, 5.59. Found: C, 66.41; H, 5.44.

Ethyl (1-Methoxy-5-oxo-5H-benzocyclohepten-4-yloxy)acetate (8).

A mixture of **7a** (2.0 g, 7.69 mmoles), ethanol (50 ml), and five drops of sulfuric acid was refluxed for 1.5 hours. After evaporation of the ethanol the residue was extracted with ether. The extract was washed, dried, and evaporated. The residue was chromatographed and eluted with benzene(9)-ether(1) to give **8** (1.86 g, 84%); it formed colorless needles from ethanol, mp 75-76°; ir (potassium bromide): 1750 ($\text{CO}_2\text{C}_2\text{H}_5$), 1665 cm^{-1} (CO); ^1H nmr (deuteriochloroform): δ 1.26 (t, $J = 7$ Hz, 3H, CH_2CH_3), 3.85 (s, 3H, OCH_3), 4.22 (q, $J = 7$ Hz, 2H, CH_2CH_3), 4.70 (s, 2H, CH_2CO_2), 6.48-6.89 (m, 3H, $\text{C}_7\text{-H}$, $\text{C}_8\text{-H}$, and $\text{C}_9\text{-H}$), 6.94 (d, $J = 9$ Hz, $\text{C}_2\text{-H}$ or $\text{C}_3\text{-H}$), 7.15 (d, $J = 9$ Hz, 1H, $\text{C}_2\text{-H}$ or $\text{C}_3\text{-H}$), 7.67-7.83 (m, 1H, $\text{C}_6\text{-H}$); ^{13}C nmr (deuteriochloroform): δ 14.1 (q), 56.4 (q), 61.1 (t), 69.6 (t), 111.9 (d), 118.5 (d), 125.4 (s), 126.4 (d), 128.8 (d), 131.7 (d), 132.5 (s), 133.8 (d), 149.9 (s), 152.0 (s), 169.2 (s), 190.2 (s).

Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_5$: C, 66.66; H, 5.59. Found: C, 66.41; H, 5.49.

7-Methoxycyclohepta[*cd*]benzofuran (**1a**).

A mixture of **7a** (4.0 g, 15.4 mmoles), sodium acetate (18.0 g, 220 mmoles), and acetic anhydride (60 ml) was heated at 150° for 1 hour [10]. The mixture was poured into ice-water to decompose excess of acetic anhydride and extracted with ether. The extract was washed with a 1*M* aqueous potassium hydroxide solution (30 ml x 3) then with water, dried, and evaporated. The residue was chromatographed and eluted with benzene(1)-hexane(1) to give **1a** (2.8 g, 92%) as a red oil, bp 128-130° (1 Torr); ¹H nmr (deuteriochloroform): δ 3.72 (s, 3H, OCH₃), 5.10-5.28 (m, 2H, C₃-H, C₄-H, C₅-H, or C₆-H), 5.70-5.90 (m, 1H, C₃-H, C₄-H, C₅-H, or C₆-H), 6.14-6.38 (m, 1H, C₃-H, C₄-H, C₅-H, or C₆-H), 6.56 (d, J = 9 Hz, 1H, C₈-H or C₉-H), 6.86 (d, J = 9 Hz, 1H, C₈-H or C₉-H), 6.91 (s, 1H, C₂-H); ¹³C nmr (deuteriochloroform): δ 56.9 (q), 111.7 (d), 111.8 (d), 123.1 (s), 125.0 (s), 125.6 (d), 126.7 (d), 127.0 (d), 131.6 (s), 138.5 (d), 150.5 (s), 151.6 (s).

Anal. Calcd. for C₁₃H₁₀O₂: C, 78.77; H, 5.08. Found: C, 78.78; H, 5.20.

7-Methoxy-2-methylcyclohepta[*cd*]benzofuran (**1b**).

Compound **1b** (90%) was prepared from **7b** in a manner similar to the synthesis of **1a**; it formed red plates from methanol, mp 66-67°; ¹H nmr (deuteriochloroform): δ 2.09 (s, 3H, CH₃), 3.68 (s, 3H, OCH₃), 4.98-5.35 (m, 2H, C₃-H, C₄-H, C₅-H, or C₆-H), 5.59-5.74 (m, 1H, C₃-H, C₄-H, C₅-H, or C₆-H), 6.05-6.21 (m, 1H, C₃-H, C₄-H, C₅-H, or C₆-H), 6.42 (d, J = 9 Hz, 1H, C₈-H or C₉-H), 6.73 (d, J = 9 Hz, 1H, C₈-H or C₉-H); ¹³C nmr (deuteriochloroform): δ 11.2 (q), 57.0 (q), 110.8 (d), 111.1 (d), 119.6 (s), 122.6 (s), 124.2 (d), 126.2 (d), 126.8 (d), 133.1 (s), 147.5 (s), 149.8 (s), 150.5 (s).

Anal. Calcd. for C₁₄H₁₂O₂: C, 79.22; H, 5.70. Found: C, 78.98; H, 5.80.

2-Ethyl-7-methoxycyclohepta[*cd*]benzofuran (**1c**).

Compound **1c** (91%) was prepared from **7c** in a manner similar to the synthesis of **1a**; it formed red needles from methanol, mp 83-84°; ¹H nmr (deuteriochloroform): δ 1.15 (t, J = 7 Hz, 3H, CH₃CH₂), 2.44 (q, J = 7 Hz, 2H, CH₃CH₂), 3.69 (s, 3H, OCH₃), 5.05-5.36 (m, 2H, C₃-H, C₄-H, C₅-H, or C₆-H), 5.63-5.76 (m, 1H, C₃-H, C₄-H, C₅-H, or C₆-H), 6.07-6.19 (m, 1H, C₃-H, C₄-H, C₅-H, or C₆-H), 6.43 (d, J = 9 Hz, 1H, C₈-H or C₉-H), 6.75 (d, J = 9 Hz, 1H, C₈-H or C₉-H); ¹³C nmr (deuteriochloroform): δ 12.4 (q), 19.2 (t), 57.1 (q), 111.1 (d), 111.2 (d), 118.6 (s), 122.8 (s), 124.2 (d), 126.1 (d), 126.8 (d), 133.1 (s), 149.8 (s), 150.5 (s), 152.7 (s).

Anal. Calcd. for C₁₅H₁₄O₂: C, 79.62; H, 6.24. Found: C, 79.87; H, 6.38.

Synthesis of **1a-c** by Photocyclization.

An acetonitrile solution (700 ml) of **7a** (0.30 g, 1.15 mmoles) was deoxygenated by bubbling nitrogen gas for 1 hour and irradiated for 0.5 hour. After evaporation of the acetonitrile the residue was chromatographed and eluted with benzene to give **1a** (0.032 g, 14%). When compound **7b** was similarly irradiated for 2.5 hours **1b** was obtained in 50% yield. Irradiation of **7c** for 1.5 hours afforded **1c** in 67% yield.

Reaction of **8** with Sodium Hydride.

A mixture of **8** (0.52 g, 1.80 mmoles), 60% sodium hydride (0.36 g, 9.0 mmoles), and anhydrous dioxane (10 ml) was refluxed for 1 hour. After decomposition of the excess sodium hydride with water (10 ml) the mixture was poured into 2*M* hydrochloric acid (100 ml) and extracted with ether. The extract was washed with a 1*M* aqueous potassium carbonate solution (30 ml x 3) then with water, dried, and evaporated. The residue was chromatographed and eluted with benzene(1)-hexane(1) to give **1a** (0.19 g, 53%). 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 7-methoxycyclohepta[*cd*]benzofuran-2-carboxylic acid (**1d**, 0.15 g, 34%); it formed red plates from dioxane, mp 232-233° dec; ir (potassium bromide): 1670 cm⁻¹ (CO₂H); ¹H nmr (deuterioacetone): δ 3.84 (s, 3H, OCH₃), 5.60-5.94 (m, 2H, C₃-H, C₄-H, C₅-H, or C₆-H), 6.56-6.72 (m, 1H, C₃-H, C₄-H, C₅-H, or C₆-H), 6.87-7.02 (m, 1H, C₃-H, C₄-H, C₅-H, or C₆-H), 7.02 (d, J = 8 Hz, 1H, C₈-H or C₉-H), 7.15 (d, J = 8 Hz, 1H, C₈-H or C₉-H).

Anal. Calcd. for C₁₄H₁₀O₄: C, 69.42; H, 4.16. Found: C, 69.25; H, 4.08.

4-Hydroxy-1-methoxy-6,7,8,9-tetrahydro-5*H*-benzocycloheptene-5,9-dione (**10**).

A mixture of **9** (10.0 g, 48.5 mmoles), dimethyl sulfate (6.7 g, 53.2 mmoles), and acetone (60 ml) was refluxed for 2 hours. After evaporation of the acetone the mixture was extracted with ether. The extract was washed, dried, and evaporated. The residue was chromatographed and eluted with benzene(95)-ether(5) to give **10** (5.50 g, 52%); it formed yellow plates from methanol, mp 94-95°; ir (potassium bromide): 1710 (CO), 1645 cm⁻¹ (CO); ¹H nmr (deuteriochloroform): δ 1.90-2.21 (m, 2H, C₇-H₂), 2.75-3.00 (m, 4H, C₆-H₂ and C₈-H₂), 3.81 (s, 3H, OCH₃), 7.03 (d, J = 9 Hz, 1H, C₂-H or C₃-H), 7.24 (d, J = 9 Hz, 1H, C₂-H or C₃-H), 11.77 (s, 1H, OH); ¹³C nmr (deuteriochloroform): δ 17.3 (t), 41.9 (t), 43.5 (t), 57.9 (q), 116.5 (s), 120.7 (d), 122.6 (d), 131.0 (s), 148.3 (s), 156.3 (s), 202.4 (s), 206.6 (s).

Anal. Calcd. for C₁₂H₁₂O₄: C, 65.44; H, 5.49. Found: C, 65.50; H, 5.51.

Synthesis of **3** by Catalytic Hydrogenation of **10**.

A mixture of **10** (1.00 g, 4.55 mmoles), 10% palladium on charcoal (0.50 g), and ethanol (30 ml) was hydrogenated for 3 hours at 40°. After removal of the catalyst the ethanol was evaporated. The residue was chromatographed and eluted with benzene to give **3** (0.87 g, 93%).

Protonation of **1a** with Trifluoroacetic Acid.

Furan **1a** (27 mg, 0.14 mmole) was dissolved in deuteriochloroform (0.37 ml) in the nmr tube. To the above solution trifluoroacetic acid (0.14 ml) was added [4-6,18]. The solution turned deep green. The nmr spectrum of the solution was determined at room temperature, showing the formation of **11**; ¹H nmr (deuteriochloroform): δ 4.20 (s, 3H, OCH₃), 6.27 (s, 2H, OCH₂), 7.93 (d, J = 9 Hz, 1H, C₈-H or C₉-H), 8.15 (d, J = 9 Hz, 1H, C₈-H or C₉-H), 7.98-8.27 (m, 2H, C₄-H, C₅-H, or C₆-H), 8.63 (dd, J = 9 and 10 Hz, 1H, C₄-H, C₅-H, or C₆-H), 9.47 (d, J = 11 Hz, 1H, C₃-H).

Catalytic Hydrogenation of **1a** with Palladium on Charcoal.

A mixture of **1a** (1.00 g, 5.05 mmoles), 7% palladium on charcoal (0.5 g), and ethanol (40 ml) was hydrogenated for 1.5 hours at room temperature [4,5]. After removal of the catalyst by filtration the ethanol was evaporated. The residue was chromatographed and eluted with benzene(1)-hexane (1) to give 7-methoxy-3,4,5,6-tetrahydrocyclohepta[*cd*]benzofuran (**12**, 0.95 g, 93%) as a colorless oil. This compound was identical with an authentic sample [10] with regard to the ir and nmr spectra.

Reduction of **1a** with Sodium and Ethanol.

Compound **1a** (0.20 g, 1.01 mmoles) was dissolved in ethanol (20 ml) and the solution was kept under reflux. Sodium (1.90 g, 82.6 mmoles) was added gradually to the solution. After 40 minutes 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(1)-hexane(1). The first fraction gave **12** (0.040 g, 20%). The second fraction afforded 7-methoxy-2,2a,3,4,5,6-tetrahydrocyclohepta[*cd*]benzofuran (**13**, 0.140 g, 68%); it formed colorless needles from methanol, mp 44-45°; ¹H nmr (deuteriochloroform): δ 1.05-2.40 (m, 8H, C₃-H₂, C₄-H₂, C₅-H₂, and C₆-H₂), 3.24-3.58 (m, 1H, C_{2a}-H), 3.73 (s, 3H, OCH₃), 4.03 (dd, J = 9 and 9 Hz, 1H, C₂-H), 4.71 (dd, J = 9 and 9 Hz, 1H, C₂-H), 6.49 (d, J = 9 Hz, 1H, C₈-H or C₉-H), 6.62 (d, J = 9 Hz, 1H, C₈-H or C₉-H); ¹³C nmr (deuteriochloroform): δ 27.0 (t), 28.0 (t), 31.0 (t), 33.8 (t), 44.5 (d), 57.1 (q), 77.2 (t), 106.0 (d), 111.2 (d), 130.4 (s), 132.4 (s), 150.9 (s), 153.9 (s).

Anal. Calcd. for C₁₃H₁₆O₂: C, 76.44; H, 7.90. Found: C, 76.25; H, 7.81.

Reaction of **1a** with Tetracyanoethylene.

A mixture of **1a** (0.20 g, 1.01 mmoles), tetracyanoethylene (0.145 g, 1.13 mmoles), and benzene (10 ml) was refluxed for 3 hours [15,16]. After removal of the benzene the residue was chromatographed and eluted with benzene(95)-ether(5) to give **14** (0.29 g, 88%); it formed colorless plates from acetone-benzene, mp 194° dec; ir (potassium bromide): 2150 (CN), 2230 cm⁻¹ (CN); ¹H nmr (deuteriochloroform): δ 3.94 (s, 3H, OCH₃),

4.42-4.50 (m, 1H, C₃-H or C₆-H), 4.96-5.06 (m, 1H, C₃-H or C₆-H), 6.60-6.72 (m, 2H, C₄-H and C₅-H), 6.98 (d, J = 8 Hz, 1H, C₈-H or C₉-H), 7.44 (d, J = 8 Hz, 1H, C₈-H or C₉-H).

Anal. Calcd. for C₁₀H₁₀N₂O₂: C, 70.24; H, 3.09; N, 17.17. Found: C, 70.07; H, 3.09; N, 16.93.

Reaction of **1a** with Phosphorus Oxychloride and Dimethylformamide.

Phosphorus oxychloride (1.20 g, 7.84 mmoles) in dimethylformamide (2.0 ml) was added to **1a** (0.40 g, 2.02 mmoles) in dimethylformamide (25 ml) and the mixture was stirred for 3 hours at room temperature [21]. The mixture was poured into ice-water and stood overnight. The resulting precipitate was extracted with ether. The extract was washed, dried, and evaporated to give **1e** (1.11 g, 97%); it formed red needles from benzene-hexane, mp 133-134°; ir (potassium bromide): 1665 cm⁻¹ (CHO); ¹H nmr (deuteriochloroform): δ 3.80 (s, 3H, OCH₃), 5.63-6.01 (m, 2H, C₃-H, C₄-H, C₅-H, or C₆-H), 6.66-6.84 (m, 2H, C₃-H, C₄-H, C₅-H, or C₆-H), 6.89 (d, J = 9 Hz, 1H, C₈-H, or C₉-H), 7.05 (d, J = 9 Hz, 1H, C₈-H or C₉-H), 9.72 (s, 1H, CHO); ¹³C nmr (deuteriochloroform): δ 57.0 (q), 111.8 (d), 115.5 (d), 124.2 (d), 124.6 (s), 127.4 (d), 129.8 (d), 131.5 (s), 132.4 (d), 133.8 (s), 144.6 (s), 150.5 (s), 151.5 (s), 177.8 (d).

Anal. Calcd. for C₁₄H₁₀O₃: C, 74.33; H, 4.46. Found: C, 74.12; H, 4.60.

Reaction of **1a** with Acetyl Chloride and Stannic Chloride.

Stannic chloride (0.40 g, 1.54 mmoles) was added to a mixture of **1a** (0.20 g, 1.01 mmoles), acetyl chloride (0.20 g, 2.56 mmoles), and carbon disulfide (20 ml) under cooling with ice-water [22]. The mixture was stirred for 0.5 hour and decomposed with 6M hydrochloric acid. The products were extracted with ether. The extract was washed, dried, and evaporated. The residue was chromatographed and eluted with benzene to give **1f** (0.040 g, 16%); it formed red needles from benzene-hexane, mp 152-154°; ir (potassium bromide): 1660 cm⁻¹ (COCH₃); ¹H nmr (deuteriochloroform): δ 2.46 (s, 3H, COCH₃), 3.79 (s, 3H, OCH₃), 5.58-5.94 (m, 2H, C₃-H, C₄-H, C₅-H, or C₆-H), 6.54-7.21 (m, 2H, C₃-H, C₄-H, C₅-H, or C₆-H), 6.85 (d, J = 9 Hz, 1H, C₈-H, or C₉-H), 7.02 (d, J = 9 Hz, 1H, C₈-H, or C₉-H).

Anal. Calcd. for C₁₅H₁₂O₃: C, 74.99; H, 5.03. Found: C, 74.95; H, 5.14.

Photoreaction of **1b**.

A solution of **1b** (0.30 g, 1.42 mmoles) in acetonitrile (700 ml) was deoxygenated by bubbling nitrogen gas for 1 hour and irradiated for 2 hours [14]. After evaporation of the acetonitrile the residue was chromatographed and eluted with benzene(8)-ether(2) to give **15** (75 mg, 25%); it formed colorless needles from methanol, mp 155-158°; ir (potassium bromide): 1745 and 1710 cm⁻¹ (C=C); ¹H nmr (deuteriochloroform): δ 2.35 (s, 3H, CH₃), 3.76 (dd, J = 1 and 3 Hz, 1H, CH-CH=CH-CH), 3.86 (s, 3H, OCH₃), 4.32 (d, J = 3 Hz, 1H, CH-CH=CH-CH), 6.29 (dd, J = 1 and 3 Hz, 1H, CH=CH), 6.61 (d, J = 3 Hz, 1H, CH=CH), 6.96 (d, J = 8 Hz, 1H, Ph-H), 7.02 (d, J = 8 Hz, 1H, Ph-H); ¹³C nmr (deuteriochloroform): δ 20.6 (q), 44.5 (d), 55.9 (d), 56.0 (q), 116.0 (d), 122.3 (d), 129.6 (s), 136.2 (d), 141.3 (s), 142.9 (s), 144.3 (d), 154.4 (s), 169.4 (s), 199.5 (s).

Anal. Calcd. for C₁₄H₁₂O₂: C, 79.22; H, 5.70. Found: C, 79.02; H, 5.85.

Acknowledgement.

We thank Mr. Yoshiaki Matsuda for the elemental analyses. This work was supported by a Grant-in-Aid for Scientific Research No 61540366 from the Ministry of Education, Science and Culture.

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