Synthesis and Properties of Furo[4,3,2-*de*][1]benzopyran

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A new heterocycle, furo[4,3,2-*de*][1]benzopyran (**2**), was synthesized. A key step in the sequence was the allylic bromination of 3,4-dihydrofuro[4,3,2-*de*][1]benzopyran (**8**) to give 3-bromo-3,4-dihydrofuro[4,3,2-*de*][1]-benzopyran (**10**) using *N*-bromosuccinimide under irradiation and high dilution conditions. Bromide **10** was dealt with 1,8-diazabicyclo[5.4.0]undec-7-ene to afford compound **2**. Several reactions of **2** were examined. Protonation of **2** in trifluoroacetic acid occurred at the 2-position to form a pyrylium ion **12**. Catalytic hydrogenation of **2** with palladium on charcoal proceeded smoothly to give **8**. Reduction of **2** by sodium and ethanol afforded 3-ethyl-4-hydroxybenzofuran (**14**). Electrophilic substitutions of **2** such as formylation, acetylation, and bromination, occurred easily at the 2-position. The above results show that compound **2** has both properties of benzofuran and 4-methylenepyran.

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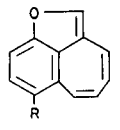
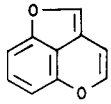
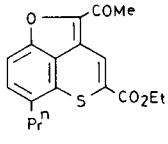
In the previous paper, we reported synthesis and reactivities of cyclohepta[*cd*]benzofurans **1a** [1] and **1b** [2]. Protonation, catalytic hydrogenation, electrophilic substitutions, and the Diels-Alder reaction of **1a,b** were examined. We found that these compounds have both properties of benzofuran and heptafulvene. Furo[4,3,2-*de*][1]benzopyran (**2**) is a pyran analogue of **1a** and will be expected to have interesting properties as compound **2** possesses a benzofuran and a 4-methylenepyran system in the same molecule. No derivative of compound **2** has been known yet. Only a thiopyran derivative **3** was prepared by Dicker *et al* [3]. In the present paper we report the synthesis and some properties of the parent heterocycle **2**.



1
a, R = H
b, R = OMe



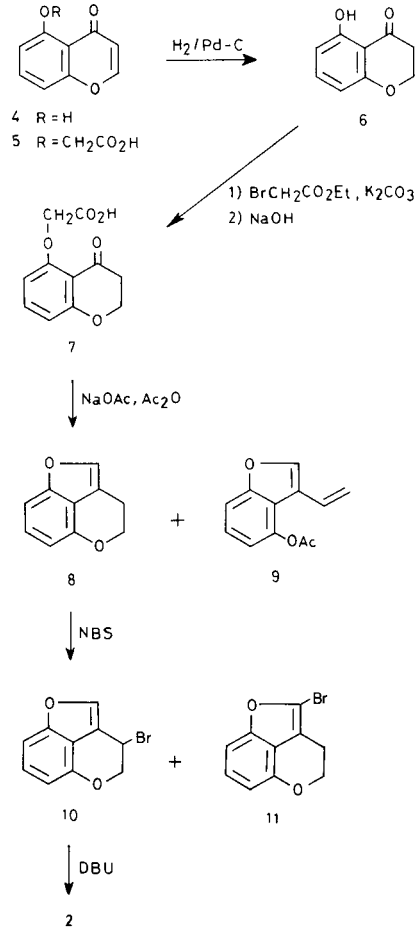
2



3

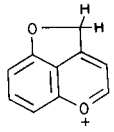
The synthesis of compound **2** is illustrated in Scheme 1. An initial attempt to prepare **2** is the condensation between the active methylene group and the carbonyl group in carboxylic acid **5**. 5-Hydroxy-4*H*-1-benzopyran-4-one (**4**), obtained from 2,6-dihydroxyacetophenone by Murata's method [4], was converted into **5** in 29% yield by heating with ethyl bromoacetate and potassium carbonate in dimethylsulfoxide (DMSO) followed by alkali hydrolysis using 2%-sodium hydroxide solution. Compound **5** was

Scheme 1

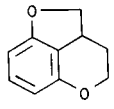


treated with sodium acetate and acetic anhydride, but the desired compound **2** was not obtained and 48% of starting material was recovered. Furthermore, reaction of ethyl ester of **5** with potassium hydroxide in dioxane did not give **2** and only hydrolyzed compound **5** (23%) was obtained. It was difficult to form the furan ring from benzopyrones because of inactivity of the carbonyl group [5].

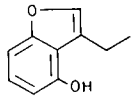
We examined another route *via* chromanone derivative **7** which has an active carbonyl group. By catalytic hydrogenation of **4** with palladium on charcoal, compound **6** was obtained in 93% yield, which was transformed into **7** in 81% yield by heating with ethyl bromoacetate and potassium carbonate in DMSO followed by saponification. By the reaction of **7** with sodium acetate and acetic anhydride, 3,4-dihydrofuro[4,3,2-*de*][1]benzopyran (**8**) and 4-acetoxy-3-vinylbenzofuran (**9**) were produced in 38 and 6% yields, respectively. Low yield of **8** is attributed to a fact that the free rotation of the carbonyl group in **7** is restricted by the pyran ring [6].



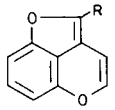
12



13



14



15 R=CHO
16 R=COMe
17 R=Br

In an attempt to introduce a double bond in the pyran ring, **8** was treated with palladium on charcoal [7] or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) [8], but dehydrogenation did not occur in either case.

An alternative attempt was carried out by brominating at the allylic position of **8** followed by dehydrobromination. It is known that bromination of 3-methylbenzofuran using *N*-bromosuccinimide (NBS) occurs at the 2-position rather than the allylic position [9]. When **8** was treated with one equivalent of NBS in carbon tetrachloride using benzoyl peroxide (BPO) as an initiator, 3-bromide **10** and 2-bromide **11** were produced in 15 and 67% yields, respectively. In this case, most of bromination also occurred in the furan ring. In order to increase the yield of **10**, bromination was carried out under various reaction conditions as shown in Table 1. It is considered that **10** is produced by the radical reaction and **11** by the ionic reaction [10]. By the irradiation with the light of fluorescent lamps in order to accelerate the radical reaction, the ratio of **10** was slightly increased (Entry 2). By diluting the solution by a factor of ten in an attempt to suppress the ionic reaction [11], the yield of compound **10** was increased substantially (Entry 3). Under irradiation and dilution conditions, **10** was obtained in fair yield (43%) (Entry 4). High dilution method was very effective in this case.

Table 1
Reaction of Dihydrofurobenzopyran **8** with One Equivalent of NBS under Various Conditions

Entry	Concentration of **8** (mol l^{-1})	Reaction time, hours	Ratio [b] **10**:**11**	Yield (%) **10**	**11**	**8**
1	1.33×10^{-1}	7	18:82	15	67	5
2 [a]	1.33×10^{-1}	3	32:68	24	50	0
3	1.33×10^{-2}	6	65:35	38	20	10
4 [a]	1.33×10^{-2}	2	80:20	43	11	10

[a] Reaction mixture was refluxed over two fluorescent lamps. [b] The ratio **10** : **11** was determined by the ^{1}H nmr spectrum of the mixture obtained by column chromatography.

Dehydrobromination of **10** with 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) gave furo[4,3,2-*de*][1] benzopyran (**2**) as unstable colorless needles in 85% yield. The structure of **2** was confirmed by the spectral data. The ir spectrum showed the absorptions at 1663 cm^{-1} due to the double bond of the pyran ring and 864 cm^{-1} due to the furan ring. The ^{1}H nmr spectrum (deuteriochloroform) exhibited the signals at δ 5.84 (d, J = 6 Hz, 1H) and δ 6.59 (d, J = 6 Hz, 1H) in the olefinic region due to the protons of the pyran ring and δ 7.02 (s, 1H) in the aromatic region due to the proton of the furan ring. Although **2** is completely changed to colorless polymeric materials within a few days at room temperature under nitrogen, it could be stored with no change at $-20°$. Compound **2** is stable in polar solvents such as ethanol and acetone rather than nonpolar solvents such as benzene and carbon tetrachloride.

Next, several reactions of compound **2** were examined in order to clarify the properties of **2**. Compound **2** was dissolved in trifluoroacetic acid to give deep green solution. Its ^{1}H nmr spectrum (trifluoroacetic acid) exhibited the signals at δ 6.32 (s, 2H) due to the methylene protons and at δ 8.06 (d, J = 5 Hz, 1H) and δ 9.25 (d, J = 5 Hz, 1H) due to the protons of the pyran ring, values further downfield from those shown by the unprotonated species **2** (δ 5.84 and 6.59), indicating the formation of a pyrylium ion **12**. The deep green solution was poured into water, but the starting material **2** could not be recovered and only polymeric materials were obtained. Forming a pyrylium ion in acidic media is a characteristic property of 4-methylenepyran [12]. It is reported that a natural product which contains the structure of 4-methylenebenzopyran is readily protonated to yield a pyrylium ion in trifluoroacetic acid [13].

Catalytic hydrogenation of **2** with palladium on charcoal proceeded smoothly to give **8** at room temperature (1 at-

mosphere) for 15 minutes in 65% yield. Prolonged hydrogenation of **2** (1.5 hours) afforded tetrahydro derivative **13** in 79% yield. The results show that the double bond in the pyran ring has olefinic character and the double bond in the furan ring has aromatic character like that in benzofuran.

Furthermore, **2** was reduced by sodium-ethanol to give benzofuran **14** in 35% yield. Since **8** was converted into tetrahydro derivative **13** quantitatively under the same conditions, **8** is not the intermediate in the reduction of **2** to **14**.

Some electrophilic substitutions of **2** were examined. Compound **2** reacted with the Vilsmeier-Haack reagent (phosphoryl chloride in *N,N*-dimethylformamide (DMF) in an instant at room temperature to yield 2-formylfurobenzopyran **15** in 91% yield. Compound **2** showed very high reactivity toward this reagent. By acetylation of **2** with acetyl chloride and stannic chloride, **16** was obtained in 14% yield. Compound **15** and **16** are quite stable at room temperature owing to the electron-withdrawing effect of a formyl or an acetyl group. Bromination of **2** with bromine in diethyl ether afforded deep green polymeric products with the evolution of hydrogen bromide. The reaction of **2** with NBS without BPO in benzene for a few minutes at room temperature afforded bromide **17** as colorless needles in 76% yield, which gave green materials by polymerization within a few hours at room temperature under nitrogen. Compound **17** is stable in polar solvents rather than nonpolar solvents as the parent heterocycle **2**. From these results, compound **2** has unusually high reactivity toward electrophiles compared with cycloheptabenzofurans **1a,b** [1,2]. It is considered that this high reactivity of **2** is attributed to an electron-donating nature of the oxygen atom in the pyran ring.

In conclusion, **2** has both properties of benzofuran and 4-methylenepyran, and have high reactivity toward electrophiles. We are continuing further research to clarify the high reactivity of **2**.

EXPERIMENTAL

The melting points are uncorrected. Column chromatography was performed on silica gel (Wacogel C-200). Unless otherwise stated anhydrous sodium sulfate was employed as the drying agent. Ether refers to diethyl ether. The uv spectra were determined on a Hitachi 320 uv spectrophotometer. The ir spectra were determined on a Hitachi EPI-G or a Jasco IRA-2 grating ir spectrophotometer. The nmr spectra (^{1}H and ^{13}C nmr) were determined on a JEOL JNM-FX 90Q (90 MHz) or a Hitachi R-24B (60MHz) nmr spectrometer, using tetramethylsilane as an internal standard.

4-Oxo-4*H*-1-benzopyran-5-yloxyacetic Acid (**5**).

A mixture of **4** (4.9 g, 30.2 mmoles), ethyl bromoacetate (7.6 g, 45.5 mmoles), potassium carbonate (10.8 g, 78.3 mmoles), and dimethyl sulfoxide (39 ml) was stirred at 60° for 1 hour. The mixture was poured into water and extracted with ether. The extracts were washed, dried, and evaporated. The residue was dissolved in ethanol (25 ml) and hydrolyzed by adding a 2%-sodium hydroxide solution (75 ml). The alkaline solution was acidified with 6*M*-hydrochloric acid and the resulting precipitate was extracted with ether. The extracts were washed, dried, and evaporated to give **5** (1.9 g, 29%) as colorless needles, mp 183-184° (from acetone); ir (potassium bromide): 1760 (CO_2H), 1650 cm^{-1} (CO); ^{1}H nmr (deuterioacetone): δ 4.85 (s, 2H, OCH_2CO_2), 6.32 (d, J = 6 Hz, 1H, 3-H), 7.13 (dd, J = 8 and 1 Hz, 1H, ArH), 7.26 (dd, J = 8 and 1 Hz, 1H, ArH), 7.76 (dd, J = 8 and 8 Hz, 1H, ArH), 8.12 (d, J = 6 Hz, 1H, 2-H); ^{13}C nmr (deuterioacetone): δ 69.6 (t), 112.7 (d), 113.3 (d), 114.7 (d), 116.7 (s), 135.7 (d), 156.6 (d), 158.6 (s), 159.0 (s), 169.4 (s), 178.8 (s).

Anal. Calcd. for $C_{11}H_8O_5$: C, 60.01; H, 3.66. Found: C, 59.77; H, 3.75.

5-Hydroxy-3,4-dihydro-2*H*-1-benzopyran-4-one (**6**).

A mixture of **4** (11.0 g, 67.9 mmoles), 10% palladium on charcoal (2.4 g), and ethanol (400 ml) was stirred at 60° under hydrogen (5 atmosphere) for 80 minutes. After removal of the catalyst by filtration ethanol was evaporated. The residue was distilled under reduced pressure to give **6** (10.3 g, 93%), bp 87° (0.9 Torr); it formed yellow needles, mp 27-28°; ir (potassium bromide): 1640 cm^{-1} (CO); ^{1}H nmr (deuteriochloroform): δ 2.80 (t, J = 6 Hz, 2H, 3-H_2), 4.46 (t, J = 6 Hz, 2H, 2-H_2), 6.39 (dd, J = 8 and 1 Hz, 1H, ArH), 6.47 (dd, J = 8 and 1 Hz, 1H, ArH), 7.32 (dd, J = 8 and 8 Hz, 1H, ArH), 11.70 (s, 1H, OH); ^{13}C nmr (deuteriochloroform): δ 37.0 (t), 66.4 (t), 107.2 (d), 108.5 (s), 109.2 (d), 138.0 (d), 161.8 (s), 162.2 (s), 197.9 (s).

Anal. Calcd. for $C_9H_8O_3$: C, 65.85; H, 4.91. Found: C, 65.77; H, 5.00.

4-Oxo-3,4-dihydro-2*H*-1-benzopyran-5-yloxyacetic Acid (**7**).

Compound **7** (81%) was prepared from **6** in a manner similar to the synthesis of **5**; it formed colorless needles, mp 158-160° (from acetone); ir (potassium bromide): 1780, 1750 (CO_2H), 1660 cm^{-1} (CO); ^{1}H nmr (deuteriochloroform): δ 2.85 (t, J = 6 Hz, 2H, 3-H_2), 4.54 (t, J = 6 Hz, 2H, 2-H_2), 4.69 (s, 2H, OCH_2CO_2), 6.49 (dd, J = 8 and 1 Hz, 1H, ArH), 6.72 (dd, J = 8 and 1 Hz, 1H, ArH), 7.46 (dd, J = 8 and 8 Hz, 1H, ArH); ^{13}C nmr (deuteriochloroform): δ 38.7 (t), 66.8 (t), 67.8 (t), 107.2 (d), 112.2 (s), 112.6 (d), 137.0 (d), 158.4 (s), 163.9 (s), 168.6 (s), 192.5 (s).

Anal. Calcd. for $C_{11}H_{10}O_5$: C, 59.46; H, 4.54. Found: C, 59.66; H, 4.78.

Reaction of **7** with Sodium Acetate in Acetic Anhydride.

A mixture of **7** (0.88 g, 4.00 mmoles), acetic anhydride (15 ml), and sodium acetate (4.6 g, 56.1 mmoles) was refluxed at 150° for 8 hours. The mixture was poured into ice-water, stirred for 10 minutes to decompose the excess of acetic anhydride, and extracted with ether. The extracts were washed with aqueous 10%-potassium carbonate and then with water, dried, and evaporated. The resulting oil was chromatographed and eluted with benzene. The first fraction gave 3,4-dihydrofuro[4,3,2-*de*][1]-benzopyran (**8**) (0.239 g, 38%) as a colorless oil, bp 74° (0.6 Torr); ir (neat): 842 cm^{-1} (furan ring); ^{1}H nmr (deuteriochloroform): δ 3.00 (td, J = 6 and 1 Hz, 2H, 3-H_2), 4.34 (t, J = 6 Hz, 2H, 4-H_2), 6.64 (dd, J = 8 and 1 Hz, 1H, ArH), 6.99 (dd, J = 8 and 1 Hz, 1H, ArH), 7.16 (dd, J = 8 and 8 Hz, 1H, ArH), 7.23 (t, J = 1 Hz, 1H, 2-H); ^{13}C nmr (deuteriochloroform): δ 22.0 (t), 67.8 (t), 103.9 (d), 106.1 (d), 111.4 (s), 117.8 (s), 125.9 (d), 136.3 (d), 151.6 (s), 154.3 (s).

Anal. Calcd. for $C_{10}H_6O_2$: C, 74.99; H, 5.03. Found: C, 74.87; H, 5.05.

The second fraction afforded 4-acetoxy-3-vinylbenzofuran (**9**) (0.046 g, 6%) as a colorless oil, bp 150° (1.8 Torr); ir (neat): 1780, 1770 (OAc), 870 cm^{-1} (furan ring); ^1H nmr (deuteriochloroform): δ 2.33 (s, 3H, CH_3CO_2), 5.30 (dd, J = 11 and 2 Hz, 1H, $CH=CH_cH_t$), 5.64 (dd, J = 18 and 2 Hz, 1H, $CH=CH_cH_t$), 6.73 (dd, J = 18 and 11 Hz, 1H, $CH=CH_2$), 6.98 (dd, J = 7 and 2 Hz, 1H, ArH), 7.17-7.41 (m, 2H, ArH), 7.65 (s, 1H, 2-H); ^{13}C nmr (deuteriochloroform): δ 20.8 (q), 109.5 (d), 116.3 (d), 116.4 (t), 119.5 (s), 124.7 (d), 125.9 (d), 141.9 (d), 144.4 (s), 157.0 (s), 168.9 (s).

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98. Found: C, 71.20; H, 5.08.

Reaction of **8** with NBS.

NBS (0.538 g, 3.03 mmoles) and BPO (0.015 g) were added to **8** (0.479 g, 3.00 mmoles) in carbon tetrachloride (23 ml) and the mixture was refluxed at 95° for 7 hours. The insoluble materials were removed by filtration. The filtrate was washed with aqueous 3%-sodium sulfite and with water, dried, and evaporated. The residue was chromatographed and eluted with benzene-hexane (1:4). The first fraction gave the mixture of 3-bromo-3,4-dihydrofuro[4,3,2-*de*][1]benzopyran (**10**) (0.108 g, 15%) and 2-bromo-3,4-dihydrofuro[4,3,2-*de*][1]benzopyran (**11**) (0.481 g, 67%). The yields of **10** and **11** were determined by ^1H nmr spectrometry. Compound **10** and **11** were partially separated by careful chromatography eluting with benzene-hexane (1:4). Compound **10**, colorless needles, mp 94-95° (from hexane); ir (potassium bromide): 887 cm^{-1} (furan ring); ^1H nmr (deuteriochloroform): δ 4.27-4.64 (m, 2H, 4-H_2), 5.37 (dd, J = 4 and 4 Hz, 1H, 3-H), 6.73 (dd, J = 8 and 1 Hz, 1H, ArH), 7.04 (dd, J = 8 and 1 Hz, 1H, ArH), 7.22 (dd, J = 8 and 8 Hz, 1H, ArH), 7.47 (s, 1H, 2-H); ^{13}C nmr (deuteriochloroform): δ 36.0 (d), 73.2 (t), 104.8 (d), 107.0 (d), 114.8 (s), 115.8 (s), 126.6 (d), 138.5 (d), 150.1 (s), 154.0 (s).

Anal. Calcd. for $C_{10}H_7O_2Br$: C, 50.24; H, 2.95. Found: C, 50.36; H, 3.01.

Compound **11**, colorless needles, mp 21-21.5°; ^1H nmr (deuteriochloroform): δ 2.91 (t, J = 6 Hz, 2H, 3-H_2), 4.34 (t, J = 6 Hz, 2H, 4-H_2), 6.64 (dd, J = 8 and 1 Hz, 1H, ArH), 6.94 (dd, J = 8 and 1 Hz, 1H, ArH), 7.12 (dd, J = 8 and 8 Hz, 1H, ArH); ^{13}C nmr (deuteriochloroform); δ 21.9 (t), 67.4 (t), 103.5 (d), 106.9 (d), 111.7 (s), 118.6 (s), 118.7 (s), 125.7 (d), 150.2 (s), 154.6 (s).

Anal. Calcd. for $C_{10}H_7O_2Br$: C, 50.24; H, 2.95. Found: C, 50.21; H, 2.92.

The second fraction afforded the starting material **8** (0.026 g, 5%) (Table 1, Entry 1).

Furo[4,3,2-*de*][1]benzopyran (**2**).

A mixture of **10** (100 mg, 0.42 mmole), benzene (0.21 ml), and DBU (0.11 ml) was heated at 60° for 30 minutes. The mixture was chromatographed and eluted with benzene-hexane (1:4). The benzene-hexane solution was carefully coevaporated several times with ethanol without complete evaporation at 50° and finally ethanol was removed under reduced pressure at 0° to give **2** (56 mg, 85%) as colorless needles, attempted recrystallization caused polymerization, mp 56-57°; uv (ethanol): λ max 223 (ε 23400), 258 (9600), 266 (8800), 287 nm (5300); ir (potassium bromide): 1663 (C=C), 864 cm^{-1} (furan ring); ^1H nmr (deuteriochloroform): δ 5.84 (d, J = 6 Hz, 1H, 3-H), 6.51 (dd, J = 8 and 1 Hz, 1H, ArH), 6.59 (d, J = 6 Hz, 1H, 4-H), 6.87 (dd, J = 8 and 1 Hz, 1H, ArH), 7.02 (s, 1H, 2-H), 7.10 (dd, J = 8 and 8 Hz, 1H, ArH); ^{13}C nmr (deuterioacetone); δ 100.3 (d), 105.3 (d), 106.3 (d), 111.8 (s), 120.6 (s), 128.2 (d), 132.7 (d), 146.3 (d), 150.1 (s), 155.2 (s).

Anal. Calcd. for $C_{10}H_6O_2$: C, 75.94; H, 3.82. Found: C, 76.22; H, 3.71.

Protonation of **2** with Trifluoroacetic Acid.

Compound **2** (31 mg, 0.20 mmole) was dissolved in trifluoroacetic acid (0.37 ml) in the nmr tube. The solution turned deep green. The nmr spectrum of the solution was determined at room temperature, showing the formation of the pyrylium ion **12**, ^1H nmr (trifluoroacetic acid): δ 6.32 (s, 2H, OCH_2), 7.52 (d, J = 8 Hz, 1H, ArH), 7.73 (d, J = 8 Hz, 1H, ArH), 8.06 (d, J = 5 Hz, 1H, 3-H), 8.62 (dd, J = 8 and 8 Hz, 1H, ArH), 9.25 (d, J = 5 Hz, 1H, 4-H).

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

A mixture of **2** (100 mg, 0.63 mmole), 10% palladium on charcoal (63 mg), and ethanol (6.0 ml) was stirred at room temperature under hydrogen (1 atmosphere) for 15 minutes. After removal of the catalyst by filtration ethanol was evaporated. The residue was chromatographed and eluted with benzene to give **8** (65 mg, 65%). Prolonged hydrogenation of **2** (1.5 hours) gave 2,2a,3,4-tetrahydrofuro[4,3,2-*de*][1]benzopyran (**13**) (81 mg, 79%) as colorless needles, mp 67-68° (from hexane); ^1H nmr (deuteriochloroform): δ 1.40-2.26 (m, 2H, 3-H_2), 3.20-3.60 (m, 1H, 2a-H), 3.87-4.87 (m, 4H, 2- and 4-H_2), 6.32 (dd, J = 8 and 1 Hz, 2H, ArH), and 6.96 (dd, J = 8 and 8 Hz, 1H, ArH); ^{13}C nmr (deuteriochloroform): δ 26.4 (t), 34.9 (d), 66.8 (t), 79.9 (t), 101.5 (d), 106.9 (d), 113.5 (s), 129.5 (d), 152.9 (s), 160.4 (s).

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 73.77; H, 5.98.

Reduction of **2** with Sodium and Ethanol.

To a solution of **2** (31 mg, 0.20 mmole) in ethanol (3.9 ml) was added portionwise small pieces of sodium (373 mg, 16.2 mmole) and the mixture was kept at room temperature for 3 hours. The mixture was poured into ice-water, acidified with 6*M*-hydrochloric acid and extracted with ether. The extracts were washed, dried, and evaporated. The residue was chromatographed and eluted with benzene to give 3-ethyl-4-hydroxybenzofuran (**14**) (11 mg, 35%) as a colorless viscous oil; ir (potassium bromide): 3400 cm^{-1} (OH); ^1H nmr (deuteriochloroform): δ 1.30 (t, J = 7 Hz, 3H, CH_2CH_3), 2.83 (qd, J = 7 and 1 Hz, 2H, CH_2CH_3), 5.20 (br s, 1H, OH), 6.29-6.63 (m, 1H, ArH), 6.87-7.09 (m, 2H, ArH), 7.23 (t, J = 1 Hz, 1H, 2-H).

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 73.76; H, 6.42.

Formylation of **2** with Phosphoryl Chloride and DMF.

To a solution of **2** (50 mg, 0.32 mmole) in DMF (0.20 ml) was added phosphoryl chloride (220 mg, 1.43 mmoles) in DMF (0.20 ml). The mixture was stirred for 10 minutes at room temperature, poured into ice-water (12 ml) and neutralized with sodium hydrogencarbonate. The mixture was allowed to stand at room temperature for 2 hours and the resulting precipitate was extracted with ether. The extracts were washed, dried, and evaporated. The residue was chromatographed and eluted with benzene-ether (10:1) to give 2-formylfuro[4,3,2-*de*][1]benzopyran (**15**) (53 mg, 91%) as yellow needles, mp 136-137° (from ethanol); uv (ethanol): λ max 224 (ε 19400), 243 (8100), 252 (6800), 262 (5700), 292 (10400), 358 nm (15000); ir (potassium bromide): 1655 cm^{-1}

(CHO); ^{1}H nmr (deuteriochloroform): δ 6.43 (d, J = 6 Hz, 1H, 3-H), 6.71 (d, J = 8 Hz, 1H, ArH), 6.99 (d, J = 8 Hz, 1H, ArH), 7.10 (d, J = 6 Hz, 1H, 4-H), 7.40 (dd, J = 8 and 8 Hz, 1H, ArH), 9.70 (s, 1H, CHO); ^{13}C nmr (deuteriochloroform): δ 100.1 (d), 105.5 (d), 106.2 (d), 119.8 (s), 122.1 (s), 132.0 (d), 141.2 (s), 150.3 (s), 150.3 (d), 154.6 (s), 176.8 (d).

Anal. Calcd. for $C_{11}H_6O_3$: C, 70.97; H, 3.25. Found: C, 70.93; H, 3.27.

Reaction of **2** with Acetyl Chloride and Stannic Chloride.

Compound **2** (50 mg, 0.32 mmole) in carbon disulfide (0.50 ml) was added to a mixture of acetyl chloride (63 mg, 0.80 mmole) and stannic chloride (127 mg, 0.49 mmole) in carbon disulfide (0.50 ml) under cooling with an ice-bath. The mixture was stirred for 30 minutes and decomposed with 6*M*-hydrochloric acid. The products were extracted with ether. The extracts were washed, dried, and evaporated. The residue was chromatographed and eluted with benzene-ether (15:1) to give 2-acetylfuro[4,3,2-*de*][1]-benzopyran (**16**) (9 mg, 14%) as yellow needles, mp 134-138° dec; uv (ethanol): λ max 222 (ε 15700), 241 (8000), 253 (6100), 263 (5400), 288 (6900), 350 nm (10500); ir (potassium bromide): 1647 cm^{-1} (COMe); ^{1}H nmr (deuteriochloroform): δ 2.50 (s, 3H, $COCH_3$), 6.45 (d, J = 6 Hz, 1H, 3-H), 6.70 (d, J = 8 Hz, 1H, ArH), 6.99 (d, J = 8 Hz, 1H, ArH), 7.03 (d, J = 6 Hz, 1H, 4-H), 7.39 (d, J = 8 and 8 Hz, 1H, ArH).

Anal. Calcd. for $C_{12}H_8O_3$: C, 72.00; H, 4.03. Found: C, 71.83; H, 3.84.

Reaction of **2** with NBS.

NBS (31 mg, 0.17 mmole) was added to **2** (27 mg, 0.17 mmole) in benzene (1.3 ml). The mixture was stirred at room temperature for 30 minutes and then treated with triethylamine (0.079 ml) to restrict decomposition of the product. The mixture was chromatographed and eluted with benzene-hexane (1:4). The eluent was evaporated carefully in a manner described in the synthesis of **2** to give 2-bromofuro[4,3,2-*de*][1]benzopyran (**17**) (31 mg, 76%) as colorless needles, attempted recrystallization caused polymerization, mp 37-45° dec; uv (ethanol) λ max 228 (ε 17300), 260 (7800), 267 (7000), 292 nm (5200); ir (potassium bromide): 1663 cm^{-1} (C=C); ^{1}H nmr (deuterioacetone): δ 5.94 (d, J = 6 Hz, 1H, 3-H), 6.65 (dd, J = 8 and 1 Hz, 1H, ArH), 6.90 (d, J = 6 Hz, 1H, 4-H), 6.98 (dd, J = 8 and 1Hz, 1H, ArH), 7.24 (dd, J = 8 and 8 Hz, 1H, ArH).

Anal. Calcd. for $C_{10}H_5O_2Br$: C, 50.67; H, 2.13. Found: C, 50.44; H, 2.30.

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