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Phenanthro[4,5-*bcd*]furan Derivatives. IV. A Synthesis of Phenanthro[4,5-*bcd*]furan

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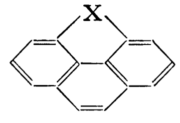
Phenanthro[4,5-*bcd*]furan was synthesized from 1,2,3,8,9,9a-hexahydrophenanthro[4,5-*bcd*]furan-3-ol by dehydrogenation with palladium–charcoal. Some chemical reactivities and spectral properties of phenanthro[4,5-*bcd*]furan were investigated and compared with those of phenantherene and dibenzofuran. The results suggest that phenanthro[4,5-*bcd*]furan has the chemical properties of both phenanthrene and dibenzofuran, and does not have a large strain in the fused-ring system. Also, the reactivities of 1,2,3,8,9,9a-hexahydrophenanthro[4,5-*bcd*]furan-3-one were explored.

Compounds such as Formula **1** have bridged atoms (C, N, S, O) which link the 4 and 5-positions in phenanthrene. The synthetic methods of these compounds except for X=O were early reported in the literature.



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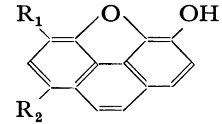

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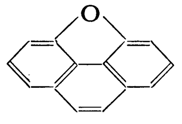


3

1a: X=C
1b: X=N
1c: X=S
1d: X=O(**3**)

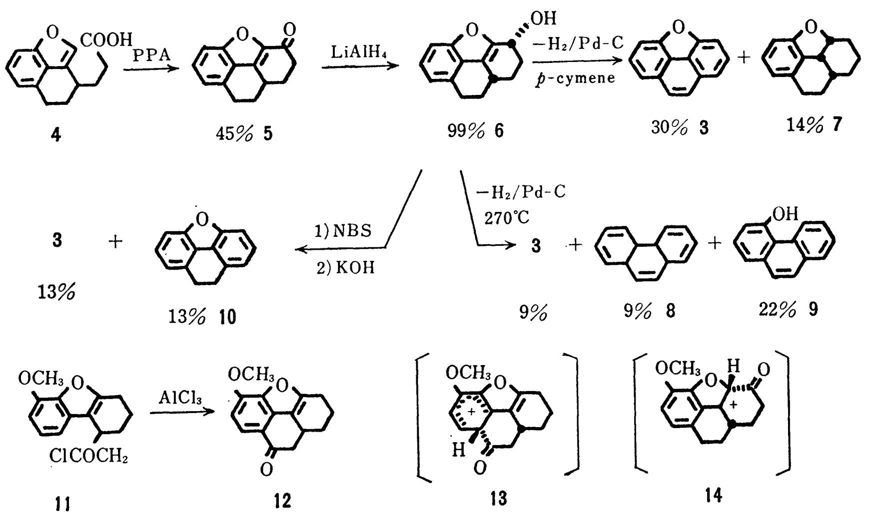
For example, phenanthro[4,5-*bcd*]thiophene (**1c**; X=S)[1] was prepared by heating phenanthrene with hydrogen sulfide at 630 °C in the presence of an alumina–chromia–magnesia catalyst. Also, phenanthro[4,5-*bcd*]-pyrrole (**1b**; X=N)[2] was similarly obtained from 4-phenanthrylamine. On the other hand, when X was a carbon atom 4*H*-cyclopenta[*def*]phenanthrene (**1a**; X=C)[3] was synthesized by the intramolecular cyclization of 3-(1-acenaphthenyl)propionic acid, followed by the reduction of the carbonyl group and then dehydrogenation. In the case of X=O, Compound **3** is termed phenanthro[4,5-*bcd*]furan and is a fundamental skeleton of morphine. Though the syntheses of **2** (R_1=R_2=H; R_1=OCH_3, R_2=H; R_1=H, R_2=OCH_3)[4–6] have already reported by us, the fundamental skeleton (**3**) has not yet been synthesized. It is said that the ring system of **3** has an inherent strain because of ether linkage between the 4 and 5-positions in phenanthrene. Therefore, we attempted to prepare phenanthro[4,5-*bcd*]furan (**3**) and discussed the strain in the phenanthro[4,5-*bcd*]furan ring by comparing the chemical reactivities and physical properties of **3** with those of phenanthrene, dibenzofuran, and other related compounds.

Results and Discussion

The synthesis of phenanthro[4,5-*bcd*]furan (**3**) was attempted in three ways; the routes are shown in Scheme 1. For the synthesis of **3** 1,2,3,8,9,9a-hexahydrophenanthro[4,5-*bcd*]furan-3-one (**5**)[4] was employed as an important intermediate. When **5** was reduced with lithium aluminum hydride, only one product, 1,2,3,8,9,9a-hexahydrophenanthro[4,5-*bcd*]furan-3-ol (**6**), was obtained. Although the formation of diastereoisomers is possible by the attack of lithium aluminum hydride on the carbonyl group from both sides, it seems that only one-sided attack from the less hindered face occurred preferentially because of steric requirements. A similar asymmetric synthesis has been reported[7] in the reduction of 1-bromocodeine to codeine with lithium aluminum hydride. It appears that the structure of the alcohol is as is shown in Formula **6** judging from the molecular model and the NMR spectrum. The methine proton on a carbon atom at the 3-position of **6** has absorptions (multiplet) at δ 4.85—5.06, and the coupling pattern is similar to that of the methine proton on a carbon atom at the 3-position of **16** (*vide infra*). This suggests that the configurations of the two methine protons of **6** and **16** are the same.

By the dehydrogenation of **6** with palladium–charcoal in *p*-cymene, the desired phenanthro[4,5-*bcd*]furan (**3**) was obtained in a 30% yield, along with 1,2,3,3a,8,9,9a,9b-octahydrophenanthro[4,5-*bcd*]furan (**7**; 14% yield). The structure of **3** was confirmed by the elemental analysis and by its spectral properties (see Experimental). When **6** was heated with palladium-charcoal without a solvent at 270 °C, three kinds of products were obtained; phenanthro[4,5-*bcd*]furan (**3**; 9%), phenanthrene (**8**; 9%), and 4-phenanthrol (**9**; 22%). As the separation of **3** and **8** was fairly difficult, the ratio was determined by gas chromatography. This suggests that the ether bridge is easy to cleave at a high temperature. The reaction of **6** with *N*-bromosuccinimide gave a mixture of two products after the elimination of hydrogen bromide with potassium hydroxide. The NMR spectrum of the mixture showed that it consisted of phenanthro[4,5-*bcd*]furan (**3**; 13% yield) and 8,9-dihydrophenanthro[4,5-*bcd*]furan (**10**; 13% yield). Therefore, in all three methods the yield of the aromatization of **6** was the best when it was carried out in *p*-cymene.

Dendy *et al.*[8] attempted to cyclize **11** to a phenanthro[4,5-*bcd*]furan derivative (**12**) by means of a Friedel-Crafts reaction. However, the yields was very low, and so they abandoned the subsequent synthesis of morphenol (**2**; R_1=R_2=H). In the case of naphtho[1,8-*bc*]furan derivatives (**4**), the cyclization occurred easily to give **5** in good yields.[4] The structure of **5** and **12** are similar to each other; therefore, the ring strains of the two compounds seem almost the same, if present at all. In the Friedel-Crafts reaction (**11**→**12**) an sp^2

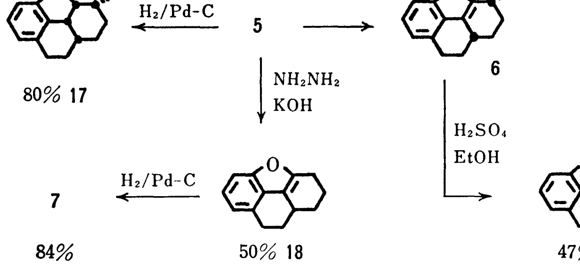


Scheme 1.

hybrid orbital of a carbon atom in the benzene ring must be changed to an sp^3 hybrid orbital in an intermediate, as is shown in Formula **13**. The consideration of a molecular model suggests that the conformation of the intermediate **13** must be cup-shaped and have a strain. On the other hand, in the case of **4** the cyclization occurs without a large deformation of the **4** molecule because the side chain of propionic acid is situated at a very favorable position for the cyclization reaction. From these consideration, it seems that the low yield of **12** is due to the strain in the intermediate, **13**, rather than to that in the product, **12**. If the carbon-carbon double bond in the furan ring of **11** is hydrogenated, the cyclization would become easy, for the side chain of acetic acid could closely approach the benzene ring.

Some chemical reactivities on **5** are shown in Scheme 2. Compound **6** dissolved in ethanol was converted to two products (**15** and **16**) by the action of sulfuric acid. The two products are diastereoisomers to each other, and the yields are 47 and 38% respectively. The structures of **15** and **16** were confirmed by comparing the NMR spectra with that of **6**. The catalytic hydrogenation of **5** with palladium–charcoal gave 1,2,3,3a,-8,9,9a,9b-octahydrophenanthro[4,5-*bcd*]furan-3-ol (**17**) in an 81% yield. The infrared spectrum of **17** shows an absorption due to a monomeric hydroxyl group at 3580 cm^{-1}. This suggests that a hydroxyl group is present in the cup-shaped molecule and that the juncture is all *cis*, as is shown in Formula **17**. By the Wolff-Kishner reduction of **5**, 1,2,3,8,9,9a-hexahydrophenanthro[4,5-*bcd*]furan (**18**) was obtained in a 50% yield. Compound **18** was hydrogenated with palladium–charcoal to give 1,2,3,3a,8,9,9a-octahydrophenanthro-[4,5-*bcd*]furan (**7**) in an 84% yield. The structure of **7** must be a *cis-cis* juncture, as is shown in Formula **7**, because **18** is easy to approach from the less-hindered face to the catalyst and the NMR spectrum of **7** is similar to that of **17**.

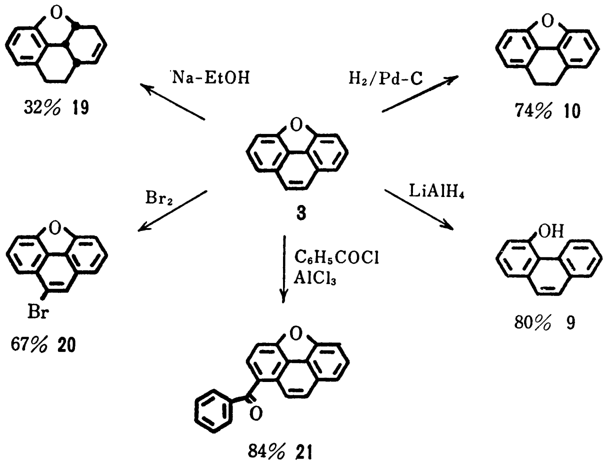
Some chemical reactivities of phenanthro[4,5-*bcd*]-furan (**3**) were investigated and compared with those of phenanthrene and dibenzofuran. The results are shown in Scheme 3. The catalytic hydrogenation of **3** with palladium–charcoal gave 8,9-dihydrophenanthro[4,5-*bcd*]furan (**10**) in a 74% yield. Under the same conditions, phenanthrene was not reduced, but it was hydrogenated to 9,10-dihydrophenanthrene under more drastic conditions (copper chromium oxide, 150—200 atm, 180 °C).[9] By the bromination of **3** with bromine, 8-bromophenanthro[4,5-*bcd*]furan (**20**) was obtained in a 67% yield. Also, phenanthrene was brominated to 9-bromophenanthrene.[12] However, the bromination of dibenzofuran gave 2-bromodibenzofuran.[13] These findings suggest that the 8,9-double bond of **3** has a considerable olefinic character and is more reactive than that in phenanthrene. When Compound **3** was heated with sodium and ethanol, 3,3a,8,9,9a,9b-hexahydrophenanthro[4,5-*bcd*]furan (**19**) was obtained in a 32% yield. Under these conditions dibenzofuran was reduced to 1,2,3,4-tetrahydrodibenzofuran,[10] but phenanthrene was not converted to 9,10-dihydro-



Scheme 2.

phenanthrene without the employment of sodium and 1-pentanol.[11] By the Friedel-Crafts reaction of **3** and benzoyl chloride with anhydrous aluminum chloride 1-benzoylphenanthro[4,5-*bcd*]furan (**21**) was obtained in an 84% yield. Under similar conditions, dibenzofuran also reacted with benzoyl chloride to give 2-benzoyldibenzofuran.[16] When **3** was treated with lithium aluminum hydride in dry ether, 4-phenanthrol (**9**) was obtained in an 80% yield. As the ether bridge in a five-membered ring is difficult to cleave with lithium aluminum hydride, the facile cleavage of the ether bridge may due to an inherent strain in the fused-ring system of **3**. In fact, dibenzofuran is not reduced under these conditions.

From these experimental results, it appears that phenanthro[4,5-*bcd*]furan has the character of both phenanthrene and dibenzofuran and is more reactive because of the ether bridge in the fused-ring system of **3**.



Scheme 3.

The ultraviolet spectrum of phenanthro[4,5-*bcd*]furan (**3**) is shown, along with that of pyrene[1] in Fig. 1. The shapes of the spectra of **3** and pyrene are very similar to each other, but the region of absorption for **3** is shifted to a shorter wavelength than that of pyrene. It is thus apparent that a non-bonding pair of electrons on the oxygen atom functions as part of the overall chromophoric π-system in phenanthro[4,5-*bcd*]furan. Also, the ultraviolet spectra of phenanthro[4,5-*bcd*]furan (**1d**; X=O), phenanthro[4,5-*bcd*]thiophene (**1c**; X=S),[1] and phenanthro[4,5-*bcd*]pyrrole (**1b**; X=N)[2,15] are shown in Fig. 2. The shapes of the three spectra are similar to one another, and in all the regions of absorptions shift to longer wavelengths as X changes from a oxygen atom to a sulfur or a nitrogen atom. This shows that interaction between the non-bonding pair of electrons on the oxygen atom and the π-electrons on the phenanthrene ring is weak in phenanthro[4,5-*bcd*]furan. In the case of X=N, the interaction is strong, while it is medium when X is a sulfur atom with *d*-orbitals. Moreover, the spectrum of pyrene is superimposable on that of phenanthro[4,5-*bcd*]thiophene.[1] The ultraviolet spectra of 8,9-dihydrophenanthro[4,5-*bcd*]furan and dibenzofuran are shown in Fig. 3. The shapes of the spectra of the corresponding pair of compounds are similar to each other. These spectral properties suggest that phenanthro[4,5-*bcd*]furan does not have a large strain in the fused-ring system.

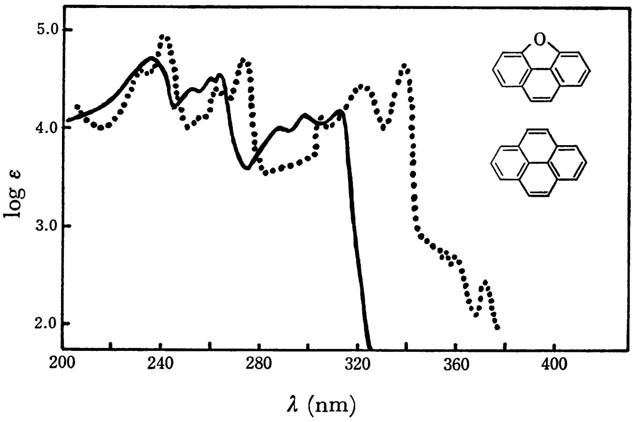


Fig. 1. Ultraviolet spectra for **3** (solid line) and pyrene (dotted line) in ethanol.

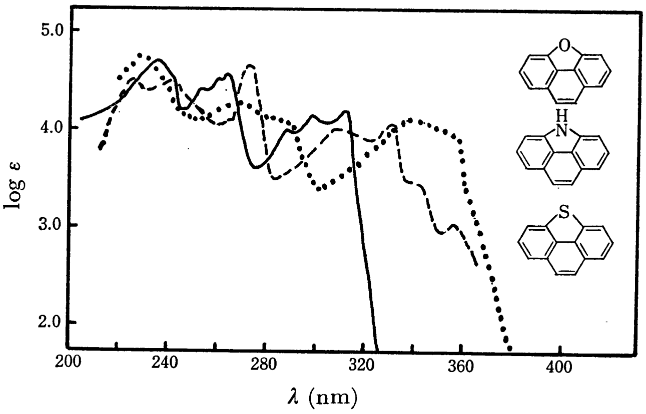


Fig. 2. Ultraviolet spectra for **3** (solid line), **1b** (X=N; dotted line), and **1c** (X=S; broken line) in ethanol.

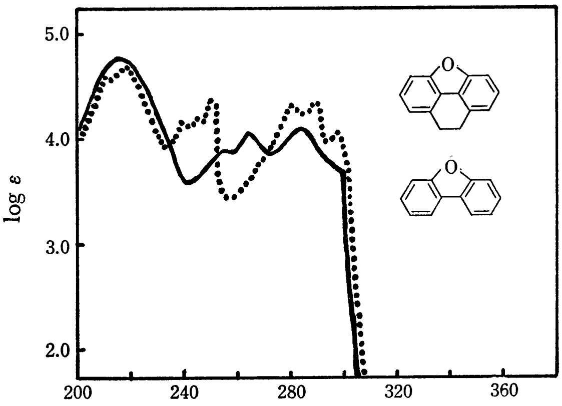


Fig. 3. Ultraviolet spectra for **10** (solid line) and dibenzofuran (dotted line) in ethanol.

Experimental

All the melting points are uncorrected. The column chromatography was performed on silica gel (WAKOGEL C-200).

Unless otherwise stated, anhydrous sodium sulfate was employed as the drying agent. The infrared absorption spectra were determined with a JASCO Model DS 402 G infrared spectrophotometer. The ultraviolet absorption spectra were determined with a Shimadzu Model UV-200 spectrophotometer. The nuclear magnetic resonance spectra were determined at 100 MHz with a JEOL Model 4H-100 NMR spectrometer, using tetramethylsilane as the internal standard.

1,2,3,8,9,9a-Hexahydrophenanthro[*4,5*-bcd]*furan-3-ol* (***6***). A mixture of **5** (2.0 g), lithium aluminum hydride (0.3 g), and dry ether (40 ml) was refluxed for 4 h. After the reaction, the excess lithium aluminum hydride was decomposed with ethyl acetate. The mixture was poured into ice water, acidified with 6 M hydrochloric acid, and extracted with ether. The ethereal layer was washed with water, dried, and then evaporated to give 2.0 g (99%) of **6** as crystals. Recrystallization from benzene gave colorless needles; mp 122—123 °C. IR (KBr): ν_{max} 746, 758, 775, 948, 996, 1023, 1052, 1075, 1240, 1350, 1635, 3300 cm^{-1}. NMR (CDCl$_3$): δ 1.02—1.43 (m, 2H, -CH$_2$-), 1.70—2.60 (m, 4H, -CH$_2$- +-CH$_2$-), 2.46 (s, 1H, OH), 2.70—2.96 (m, 3H, -CH$_2$- + =CH-), 4.85—5.06 (m, 1H, =CHO-), 6.90—7.23 (m, 3H, Ar-H). UV (EtOH): λ_{max} (ε) 210^{sh} (19500), 216 (21000), 257 (12700), 288 nm (900).

Found: C, 78.23; H, 6.71%. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59%.

Phenanthro[*4,5*-bcd]*furan* (*3*) *and 1,2,3,3a,8,9,9a,9b-Octahydrophenanthro*[*4,5*-bcd]*furan* (***7***). A mixture of **6** (3.6 g), 8% palladium-charcoal (1.0 g), and *p*-cymene (30 ml) was heated at 195 °C for 6 h under a nitrogen atmosphere. The initially produced water was removed at the first stage of the reaction. After the removal of the catalyst by filtration, the *p*-cymene was removed under reduced pressure to give an oil. The oil was chromatographed over silica gel and eluted with benzene(1)–hexane(9). From the first fraction we obtained 810 mg (30%) of **3** as crystals. Recrystallization from methanol gave colorless plates; mp 90—91 °C. IR (KBr): ν_{max} 709, 754, 816, 825, 993, 1030, 1218, 1240, 1312, 1355, 1420, 1440, 1500, 1590, 3080 cm^{-1}. NMR (CDCl$_3$): δ 7.53—7.77 (m, 6H, Ar–H), 7.92 (s, 2H, Ar–H). UV (EtOH): λ_{max} (ε) 236 (56700), 253 (26300), 260^{sh} (31000), 263 (34200), 288^{sh} (8100), 299 (12500), 313 nm (14500).

Found: C, 87.25; H, 4.27%. Calcd for $C_{14}H_8O$: C, 87.48; H, 4.20%.

By further elution with benzene(1)–hexane(1), 380 mg (14%) of **7** were obtained as crystals. Recrystallization from methanol gave colorless needles; mp 79.5—80.5 °C. IR (KBr): ν_{max} 743, 763, 855, 876, 915, 967, 1005, 1080, 1210, 1230, 1243, 1455, 1610, 1630, 2880, 2960, 3080 cm^{-1}. NMR (CDCl$_3$): δ 0.95—1.20 (m, 3H, -CH$_2$- + -CH$_2$-), 1.35—1.70 (m, 2H, -CH$_2$-), 1.78—2.00 (m, 3H, -CH$_2$- + -CH$_2$-), 2.05—2.39 (m, 1H, =CH-), 2.64 (d,d, J=6 and 10 Hz, 2H, -CH$_2$-), 3.35 (t, J=6 Hz, 1H, Ar-CH=), 4.91 (t, J=8 Hz, 1H, =CHO-), 6.56 (d, J=8 Hz, 1H, Ar-H), 6.62 (d, J=8 Hz, 1H, Ar-H), 7.00 (t, J=8 Hz, 1H, Ar-H). UV (EtOH): λ_{max} (ε) 208 (29200), 232^{sh} (4000), 275—285 nm (1600).

Found: C, 83.82; H, 8.06%. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05%.

*Dehydrogenation of **6** without a Solvent.* A mixture of **6** (1.0 g) and 8% palladium-charcoal (0.1 g) was heated at 275 °C for 1 h under a nitrogen atmosphere. After the reaction, benzene was added to the mixture and the catalyst was removed by filtration. The benzene was evaporated to give an oil. The oil was chromatographed over silica gel and eluted with benzene(1)–hexane(9). The first fraction gave 160 mg of crystals. It was composed of phenanthro[4,5-*bcd*]furan (**3**) and phenanthrene (**8**), and the **3/8** ratio was found to be 1 by gas chromatography. By the fractional recrystallization of the mixture from ethanol, a few of individual components were obtained in a pure state. However, the separation of **3** and **8** was generally difficult.

By further elution with benzene, 220 mg (22%) of 4-phenanthrol (**9**) were obtained as crystals. Recrystallization from benzene–hexane gave colorless needles; mp 112—113 °C. (lit,[14] mp 113 °C). IR (KBr): ν_{max} 716, 743, 800, 830, 1004, 1225, 1290, 1313, 1345, 1420, 1445, 1580, 3085, 3555 cm^{-1}. NMR (CDCl$_3$): δ 5.57 (s, 1H, OH), 6.81 (d,d, J=2 and 8 Hz, 1H, Ar-H), 7.17—7.90 (m, 6H, Ar-H), 7.65 (s, 2H, Ar-H). UV (EtOH): λ_{max} (ε) 213 (25000), 226 (23700), 244 (49500), 249^{sh} (44100), 275 (20900), 295^{sh} (9000), 302^{sh} (7700), 323 (2000), 338 (3300), 355 nm (4100).

Found: C, 86.32; H, 5.20%. Calcd for $C_{14}H_{10}O$: C, 86.57; H, 5.19%.

*Reaction of **6** with* N-*Bromosuccinimide.* A mixture of **6** (0.5 g), *N*-bromosuccinimide (1.0 g), and carbon tetrachloride (10 ml) was refluxed for 1 h. After the removal of the insoluble materials by filtration, the carbon tetrachloride was evaporated. To the residue potassium hydroxide (3.0 g) and ethanol (20 ml) was added, after which the mixture was refluxed for 3 h. The mixture was then poured into ice water, acidified with 6 M hydrochloric acid, and extracted with ether. The ethereal layer was washed with water, dried, and then evaporated. The resulting oil was chromatographed over silica gel and eluted with benzene(1)–hexane(9). The first fraction gave 120 mg (26%) of an oil which partially solidified. It consisted of phenanthro[4,5-*bcd*]furan (**3**) and 8,9-dihydrophenanthro[4,5-*bcd*]furan (**10**), and the **3/10** ratio was found to be 1 by a study of the NMR spectrum. The partially solidified oil was washed with methanol, and the resulting solid was recrystallized from methanol to give 10 mg (2%) of **3** as colorless plates; mp 90—91 °C.

3-Ethoxy-1,2,3,8,9,9a-hexahydro[*4,5*-bcd]*furan* (***15** and **16***). Sulfuric acid (3.0 g) was added, drop by drop, to **6** (1.5 g) in ethanol (15 ml) under cooling with ice water, after which the mixture was stirred for 3 h at 0 °C. The mixture was then poured into ice water and extracted with ether. The ethereal layer was washed with water, dried, and then evaporated to give an oil. The oil was chromatographed over silica gel and eluted with benzene. The first fraction gave 800 mg (47%) of **15** as a colorless oil. IR (neat); ν_{max} 753, 770, 780, 935, 995, 1015, 1070, 1090, 1120, 1150, 1205, 1235, 1340, 1360, 1405, 1435, 1450, 1465, 1635, 2890, 2960, 3005 cm^{-1}. NMR (CDCl$_3$): δ 1.07—1.63 (m, 2H, -CH$_2$-), 1.22 (t, J=7 Hz, 3H, -CH$_3$), 1.78—2.37 (m, 4H, -CH$_2$- + -CH$_2$-), 2.56—3.00 (m, 3H, -CH$_2$- + =CH-), 3.60—3.90 (m, 2H, -OCH$_2$-), 4.51—4.59 (m, 1H, -OCH=), 6.90—7.29 (m, 3H, Ar-H). UV (EtOH): λ_{max} (ε) 216 (23000), 256 (13100), 287 nm (1100).

Found: C, 79.10; H, 7.37%. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%.

From the second fraction, 650 mg (38%) of **16** were obtained as crystals. Recrystallization from ethanol gave colorless needles; mp 85—86 °C. IR (KBr): ν_{max} 750, 760, 773, 1092, 1120, 1245, 1350, 1400, 1465, 2890, 2970, 3005 cm^{-1}. NMR (CDCl$_3$): δ 1.06—1.48 (m, 2H, -CH$_2$-), 3.31 (t, J= 8 Hz, 3H, -CH$_3$), 1.55—2.55 (m, 4H, -CH$_2$- + -CH$_2$-), 2.67—3.07 (m, 3H, -CH$_2$- + =CH-), 3.63—4.14 (m, 2H, -OCH$_2$-), 4.59—4.77 (m, 1H, -OCH=), 6.90—7.28 (m, 3H, Ar-H). UV (EtOH): λ_{max} (ε) 216 (21800), 257 (14200), 287 nm (1000).

Found: C, 79.06; H, 7.56%. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%.

1,2,3,3a,8,9,9a,9b-Octahydrophenanthro[*4,5*-bcd]*furan-3-ol* (***17***). A mixture of **5** (1.0 g), 8% palladium-charcoal (0.3 g), and ethanol (50 ml) was shaken for 10 h at room temperature under a hydrogen atmosphere. After the removal of the catalyst by filtration, the ethanol was evaporated under reduced pressure. The resulting oil was chromatographed over silica gel and eluted with benzene(8)–ether(2) to give 0.81 g (80%) of **17** as crystals. The crystals were dissolved in hexane and recrystallized after the removal of the insoluble materials to give colorless needles; mp 74.5—76 °C. IR (KBr): $\nu_{\max}$ 534, 640, 765, 800, 838, 930, 956, 970, 1005, 1054, 1213, 1236, 1293, 1300, 1345, 1460, 1610, 1630, 2880, 2970, 3580 cm^{-1}. NMR (CDCl$_3$): δ 1.20—1.51 (m, 2H, -CH$_2$-), 1.63—2.03 (m, 2H, -CH$_2$-), 1.79 (s, 1H, OH), 2.66 (t, J=7 Hz, 2H, -CH$_2$-), 3.45 (t, J=7 Hz, 1H, Ar-CH=), 3.99—4.10 (m, 1H, -OCH=), 4.86 (d,d, J=6 and 8 Hz, 1H, -OCH=), 6.58 (d, J=8 Hz, 1H, Ar-H), 6.64 (d, J=8 Hz, 1H, Ar-H), 7.01 (t, J=8 Hz, 1H, Ar-H). UV (EtOH): $\lambda_{\max}$ (ε) 208 (28500), 276—286 nm (1600).

Found: C, 77.79; H, 7.45%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

1,2,3,8,9,9a-Hexahydrophenanthro[*4,5*-bcd]*furan* (**18**). A mixture of **5** (2.0 g), hydrazine hydrate (80%; 15 g), potassium hydroxide (28 g), and triethylene glycol (80 ml) was heated for 2 h at 140 °C and for 3.5 h at 190 °C. During the reaction, the distilled liquid was removed. After the reaction, the mixture was poured into ice water, acidified with 6 M hydrochloric acid, and extracted with ether. The ethereal layer was washed with water, dried, and then evaporated. The resulting oil was chromatographed over silica gel and eluted with benzene(1)–hexane(1) to give 0.93 g (50%) of **18** as crystals. Recrystallization from methanol gave colorless plates; mp 46—47 °C. IR (KBr): $\nu_{\max}$ 758, 777, 822, 956, 1012, 1110, 1188, 1210, 1222, 1240, 1335, 1450, 1465, 1500, 1630, 1675, 2870, 2960, 3080 cm^{-1}. NMR (CDCl$_3$): δ 0.80—1.45 (m, 2H, -CH$_2$-), 1.70—2.34 (m, 4H, -CH$_2$- + -CH$_2$-), 2.40—3.15 (m, 5H, -CH$_2$- + -CH$_2$- + =CH-), 6.85—7.20 (m, 3H, Ar-H). UV (EtOH): $\lambda_{\max}$ (ε) 217 (22900), 257 (12100), 288 nm (1000).

Found: C, 84.65; H, 7.15%. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12%.

1,2,3,3a,8,9,9a,9b-Octahydrophenanthro[*4,5*-bcd]*furan* (**7**). A mixture of **18** (0.4 g), 8% palladium-charcoal (0.3 g), and ethanol (20 ml) was shaken for 6 h at room temperature under a hydrogen atmosphere. After the removal of the catalyst by filtration, the ethanol was evaporated under reduced pressure. The resulting crystals were chromatographed over silica gel and eluted with benzene(6)–hexane(4) to give 0.34 g (84%) of **7** as crystals. Recrystallization from methanol gave colorless needles; mp 79.5—80.5 °C.

8,9-Dihydrophenanthro[*4,5*-bcd]*furan* (**10**). A mixture of **3** (0.35 g), 8% palladium-charcoal (0.3 g), and ethanol (30 ml) was shaken for 15 h at room temperature under a hydrogen atmosphere. After the removal of the catalyst by filtration, the ethanol was evaporated under reduced pressure. The resulting oil was chromatographed over silica gel and eluted with benzene(1)–hexane(9) to give 0.26 g (74%) of **10** as crystals. Recrystallization from methanol gave colorless leaflets; mp 41—42 °C. IR (KBr): $\nu_{\max}$ 773, 982, 1015, 1194, 1238, 1435, 1450, 1595, 1630, 1660, 3065, 3090 cm^{-1}. NMR (CDCl$_3$): δ 3.28 (s, 4H, -CH$_2$- + -CH$_2$-), 7.02—7.31 (m, 6H, Ar-H). UV (EtOH): $\lambda_{\max}$ (ε) 214 (49400), 227 (26300), 255$^{\text{sh}}$ (8000), 264 (12000), 285 (11200), 294$^{\text{sh}}$ (8600), 297$^{\text{sh}}$ nm (8000).

Found: C, 86.38; H, 5.18%. Calcd for $C_{14}H_{10}O$: C, 86.57; H, 5.19%.

4-Phenanthrol (**9**). A mixture of **3** (0.1 g), lithium aluminum hydride (0.1 g), and dry ether (20 ml) was refluxed for 25 h. The excess lithium aluminum hydride was then decomposed with ethyl acetate, and the mixture was poured into ice water and acidified with 6 M hydrochloric acid. The mixture was subsequently extracted with ether. The ethereal layer was washed with water, dried, and then evaporated to give an oil. The oil was chromatographed over silica gel and eluted with benzene(1)–hexane(9). The first fraction gave 50 mg (50%) of the starting material (**3**). From the second fraction we obtained 40 mg (80%) of **9** as colorless leaflets. The IR spectrum of the product was in according with that of 4-phenanthrol (**9**) obtained by the dehydrogenation of **6** without a solvent.

8-Bromophenanthro[*4,5*-bcd]*furan* (**20**). To **3** (0.2 g) in carbon tetrachloride (10 ml) we added 1.2 mol of bromine in carbon tetrachloride (10 ml), after which the mixture was stirred for 2 h at room temperature. It was then heated at 70 °C for 30 min to eliminate the hydrogen bromide. After the evaporation of carbon tetrachloride, the resulting crystals were chromatographed over silica gel and eluted with benzene(1)–hexane(9) to give 0.21 g (67%) of **20** as crystals. Recrystallization from ethanol gave colorless needles; mp 144—145 °C. IR (KBr): $\nu_{\max}$ 712, 770, 830, 866, 1036, 1188, 1235, 1300, 1345, 1420, 1465, 1505, 1590 cm^{-1}. NMR (CDCl$_3$): δ 7.53—7.88 (m, 6H, Ar-H), 8.16 (s, 1H, Ar-H). UV (EtOH): $\lambda_{\max}$ (ε) 222 (28100), 237 (45600), 258 (29600), 265 (34500), 308 (13100), 319 (13300), 337 (1900), 353 nm (200).

Found: C, 61.76; H, 2.73%. Calcd for $C_{14}H_7OBr$: C, 62.02; H, 2.60%.

3,3a,8,9,9a,9b-Hexahydrophenanthro[*4,5*-bcd]*furan* (**19**). Compound **3** (0.3 g) was dissolved in ethanol (20 ml), and the solution was heated under reflux. To the solution sodium (4.0 g) was added in limited amounts. When precipitates of sodium ethoxide were produced, additional ethanol (20 ml) was introduced into the solution and residual sodium was added. After the sodium had disappeared (1.5 h), the mixture was poured into ice water, acidified with 6 M hydrochloric acid, and extracted with ether. The ethereal layer was washed with water, dried, and then evaporated. The resulting oil was chromatographed over silica gel and eluted with benzene(1)–hexane(1) to give 0.1 g (32%) of **19** as a colorless oil. IR (neat): $\nu_{\max}$ 740, 770, 810, 864, 880, 926, 1023, 1042, 1220, 1235, 1244, 1465, 1615, 1635, 2890, 2960, 3060 cm^{-1}. NMR (CDCl$_3$): δ 1.38—1.69 (m, 1H, -CH$_2$-), 1.80—2.12 (m, 2H, -CH$_2$-), 2.17—2.31 (m, 1H, -CH$_2$-), 2.39—2.65 (m, 2H, -CH$_2$-), 2.71—2.96 (m, 1H, =CH-), 3.56 (t, J=8 Hz, 1H, Ar-CH=), 4.96—5.17 (m, 1H, -OCH=), 5.65 (s, 2H, CH=CH), 6.57 (d, J=8 Hz, 1H, Ar-H), 6.61 (d, J=8 Hz, 1H, Ar-H), 6.98 (t, J=8 Hz, 1H, Ar-H). UV (EtOH): $\lambda_{\max}$ (ε) 207 (26800), 275—284 nm (1900).

Found: C, 84.56; H, 6.98%. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12%.

1-Benzoylphenanthro[*4,5*-bcd]*furan* (**21**). To a solution of **3** (100 mg) and benzoyl chloride (110 mg) dissolved in carbon disulfide (5 ml) we added anhydrous aluminum chloride (100 mg). The mixture was then stirred for 6 h at room temperature, decomposed with dilute hydrochloric acid, and extracted with ether. The ethereal layer was washed with water, dried, and then evaporated. The resulting oil was chromatographed over silica gel and eluted with benzene(8)–hexane(2). The first fraction gave 130 mg (84%) of **21** as crystals. Recrystallization from methanol gave colorless needles; mp 126—127 °C. IR (KBr): 660, 702, 733, 756, 792, 960, 1028, 1215, 1232, 1270, 1325, 1400, 1505, 1590, 1650 cm^{-1}. NMR (CDCl$_3$): δ 7.38—7.89 (m, 9H, Ar-H), 7.99 (d, J=9 Hz, 1H, Ar-H), 8.06 (d, J=8 Hz, 1H, Ar-H), 8.41 (d, J=9 Hz, 1H, Ar-H). UV (EtOH): $\lambda_{\max}$ (ε) 207 (36200), 238 (52500), 255 (40300), 278$^{\text{sh}}$ (19500), 329 (19500).

Found: C, 84.89; H, 4.14%. Calcd for $C_{21}H_{12}O_2$: C, 85.12; H, 4.08%.

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References

1) L. H. Klemm, D. R. McCoy, and D. R. Olson, *J. Heterocycl. Chem.*, **7**, 1347 (1970).

2) O. Kruber and G. Grigoleit, *Chem. Ber.*, **87**, 1895 (1954).

3) W. E. Bachman and J. C. Sheehan, *J. Am. Chem. Soc.*, **63**, 204 (1941).

4) T. Horaguchi and T. Shimizu, *Bull. Chem. Soc. Jpn.*, **47**, 485 (1974).

5) T. Horaguchi and T. Shimizu, *Bull. Chem. Soc. Jpn.*, **48**, 488 (1975).

6) T. Shimizu, T. Horaguchi, and A. Watanabe, *Bull. Chem. Soc. Jpn.*, **46**, 1772 (1973).

7) M. Gates and G. Tschudi, *J. Am. Chem. Soc.*, **74**, 1109 (1952).

8) A. V. Dendy, J. H. P. Tyman, and W. B. Whalley, *J. Chem. Soc.*, **1963**, 4040.

9) J. R. Durland and H. Adkins, *J. Am. Chem. Soc.*, **59**, 135 (1937).

10) O. Hönigschmid, *Monatsh.*, **23**, 829 (1902).

11) G. Schroeter, H. Müller, and J. Y. S. Huang, *Chem. Ber.*, **62**, 645 (1929).

12) H. Henstock, *J. Chem. Soc.*, **119**, 55 (1921); H. Henstock, *ibid.*, **123**, 3097 (1923).

13) H. Gilman and S. Avakian, *J. Am. Chem. Soc.*, **68**, 580 (1946).

14) E. Mosettig and A. Burger, *J. Am. Chem. Soc.*, **57**, 2189 (1935).

15) M. Zander and W. H. Franke, *Chem. Ber.*, **99**, 1279 (1966).

16) R. G. Johnson, H. B. Willis, and H. Gilman, *J. Am. Chem. Soc.*, **76**, 6407 (1954); H. Gilman, P. T. Parker, J. C. Bailie, and G. E. Brown, *ibid.*, **61**, 2836 (1939).