# Phenanthro[4,5-*bcd*]furan Derivatives. VI. Some Electrophilic Substitution Reactions and Hydrogenation of 4*H*-Cyclopenta-[*def*]phenanthrene, Phenanthro[4,5-*bcd*]furan, and 4*H*-Benzo[*def*]carbazole

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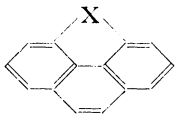
Some electrophilic substitution reactions and hydrogenation of 4*H*-cyclopenta[*def*]phenanthrene (**1a**), phenanthro[4,5-*bcd*]furan (**1b**), and 4*H*-benzo[*def*]carbazole (**1c**) have been investigated. The bromination of **1a** and **1b** with bromine gave the corresponding 8-bromo derivatives. The bromination of **1c** however gave the 1,3,5,7-tetrabromo derivative as the sole product. The benzoylation of **1a** and **1b** afforded the corresponding 1-benzoyl derivatives, but in the case of **1c**, the 1,7-dibenzoyl derivative was obtained together with the 4-benzoyl derivative. It appears that ortho- and para-orientation of the nitrogen atom in **1c** is much stronger than that of the methylene group or the oxygen atom in **1a** or **1b**. Hydrogenation of **1a**, **1b**, and **1c** with palladium–charcoal catalyst afforded the corresponding 8,9-dihydro derivatives (**4a**, **4b**, and **4c**). The reduction of **1a** and **1c** with sodium–ethanol gave **4a** and **4c**. The reduction of **1b** however gave the 3,3a,8,9,9a,9b-hexahydro derivative. It appears that facile hydrogenation of the carbon-carbon double bonds at the 8,9-positions in **1a**, **1b**, and **1c** are due to strain in the fused ring system.

The unique structures of 4*H*-cyclopenta[*def*]phenanthrene (**1a**), phenanthro[4,5-*bcd*]furan (**1b**), and 4*H*-benzo[*def*]carbazole (**1c**) are represented by the formulae **1a**—**c** which consist of phenanthrene and methylene or hetero-atom bridge linkages. Therefore, it is expected that **1a** has both the character of phenanthrene (**6**) and fluorene, **1b** has those of **6** and dibenzofuran, and **1c** has those of **6** and carbazole.



**1a**: X=$CH_2$
**1b**: X=O
**1c**: X=NH

The ultraviolet spectra of **1a**, **1b**, and **1c** are shown in Fig. 1 and those of **6** and pyrene are shown in Fig. 2. **1a** has an absorption spectrum similar to that of phenanthrene itself in the position of absorption bands and shapes suggesting that interaction (hyperconjugation) between the methylene bridge linkage and $\pi$-electrons on the phenanthrene ring is very weak. **1c** exhibits absorptions at much longer wavelengths than phenanthrene and the shapes are similar to those of pyrene which is isoelectronic with **1c** showing that interaction between non-bonding electrons on the nitrogen atom and $\pi$-electrons on the phenanthrene ring is strong. In addition the position of the absorption spectrum of **1b** lies between those of **1a** and **1c** and the shapes are similar to that of pyrene. It appears therefore that the interaction between non-bonding electrons on the oxygen atom and $\pi$-electrons on the phenanthrene ring is of medium intensity. Thus, all absorption regions of **1a**—**c** shift to longer wavelengths as X changes from the methylene group to the oxygen or the nitrogen atom. Consequently a difference in reactivity is expected upon electrophilic substitution. Additionaly it may be expected that the carbon-carbon double bonds at the 8,9-positions in **1a**, **1b**, and **1c** have abnormal character towards hydrogenation compared with the double bond at the 9,10-positions in the phenanthrene owing to the bridge linkage of X. The reactivity of phenanthro-

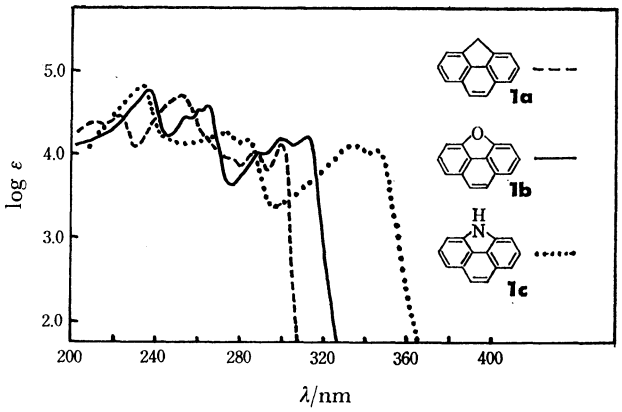



Fig. 1. The ultraviolet spectra of 4*H*-cyclopenta[*def*]-phenanthrene (**1a**), phenanthro[4,5-*bcd*]furan (**1b**), and 4*H*-benzo[*def*]carbazole (**1c**) in ethanol.

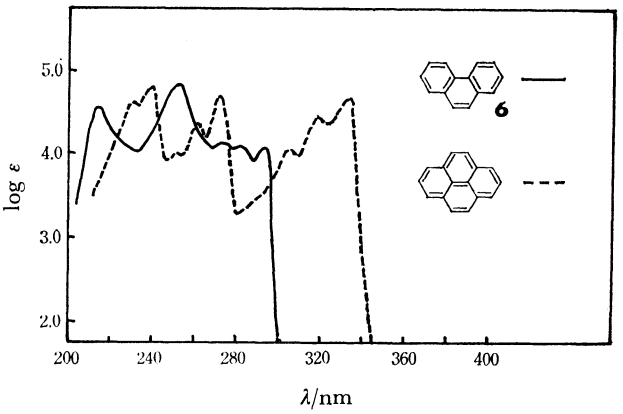



Fig. 2. The ultraviolet spectra of phenanthrene (**6**) and pyrene in ethanol.

[4,5-*bcd*]furan (**1b**) has been previously reported,[1] but there are few reports on the reactivity of **1a**[2] and **1c**.[3] Therefore, the electrophilic substitution reactions and hydrogenation of **1a** and **1c** have been examined and the reactivity of **1b** with that of **1a**, **1c**, and **6** compared.

## Results and Discussion

**1a** was synthesized by the dehydrogenation of 1-hydroxy-1,2,3,3a-tetrahydro-4*H*-cyclopenta[*def*]phenanthrene with palladium–charcoal according to the method of Bachmann.[4] **1c** was prepared in a 53% yield by heating 4-phenanthrylamine at 560 °C using calcium oxide as the catalyst in a nitrogen atmosphere; Kruber *et al.*[3a] have obtained **1c** in a 20% yield at a reaction temperature of 400 °C.

The results of several electrophilic substitution reactions and hydrogenation of **1a**, **1b**, **1c**, and phenanthrene (**6**) are summarized in Table 1.

The bromination of **1a** with bromine gave two products, 8-bromo-4*H*-cyclopenta[*def*]phenanthrene (**2a**) and 4-bromo-4*H*-cyclopenta[*def*]phenanthrene (**2e**) in 42% and 30% yields, respectively. It appears that **2a** was produced by an addition-elimination mechanism and **2e** was formed by a radical reaction. In fact, the bromination of **1a** with *N*-bromosuccinimide gave only **2e** in a 73% yield. The bromination of **1b** and phenanthrene with bromine afforded the corresponding 8-bromophenanthro[4,5-*bcd*]furan (**2b**)[1] and 9-bromophenanthrene (**7**),[5] respectively suggesting that in the case of **1a** and **1b** bromination proceeds by an addition-elimination mechanism rather than by an aromatic substitution mechanism. The reason for this is that the electron density at the ortho- and para-positions to the methylene group or the oxygen atom in **1a** or **1b** is not sufficiently high or the double bonds at the 8,9-positions in **1a** and **1b** are more reactive than the double bond at the 9,10-positions in the phenanthrene owing to strain introduced by bridge linkages as discussed below. Though the former explanation may be reasonable for the bromination of **1a**, the latter is at least plausible for the bromination of **1b** as phenanthrene-4,5-diol afforded 1,3,6,8-tetrabromophenanthrene-4,5-diol[7] by an aromatic substitution mechanism. Therefore, **1a** and **1b** have the character of phenanthrene rather than that of fluorene[8] or dibenzofuran[9] under the bromination conditions. The bromination of **1c** gave a sole product of 1,3,5,7-tetrabromo-4*H*-benzo[*def*]carbozole (**2c**) suggesting that the ortho- and para-positions to the nitrogen atom of **1c** have high electron density by strong resonance between non-bonding electrons on the nitrogen atom and $\pi$-electrons on the phenathrene ring. Therefore, the bromination of **1c** proceeds by an aromatic substitution mechanism in preference to the addition-elimination mechanism. Thus, **1c** has the

Table 1. Electrophilic substitution reactions and hydrogenation of 4*H*-cyclopenta[*def*]phenanthrene (**1a**), phenanthro[4,5-*bcd*]furan (**1b**), 4*H*-benzo[*def*]carbazole (**1c**), and phenanthrene (**6**)

| Reagents | Starting materials | | | |
|---|---|---|---|---|
| | **1a** | **1b** | **1c** | **6** |
| $Br_2$ | **2a**, **2e** | **2b** | **2c** | **7** |
| $C_6H_5COCl$, $AlCl_3$ | **3a** | **3b** | **3c**, **3g** | **8** |
| $H_2$/Pd–C | **4a** | **4b** | **4c** | no reaction |
| Na–EtOH | **4a** | **5b** | **4c** | no reaction |

character of carbazole rather than that of phenanthrene as carbazole[10] is most reactive at 3- and 6-positions under the bromination conditions. The experimental results of bromination are parallel to the shifts in the ultraviolet spectra of **1a**, **1b**, and **1c**.

The Friedel-Crafts reaction of **1a** and benzoyl chloride using aluminium chloride as the catalyst gave 1-benzoyl-4*H*-cyclopenta[*def*]phenanthrene (**3a**). The Friedel-Crafts reaction of **1b** and benzoyl chloride afforded 1-benzoylphenanthro[4,5-*bcd*]furan (**3b**).[1] The reaction of **1c** with benzoyl chloride however gave only 1,7-dibenzoyl-4*H*-benzo[*def*]carbazole (**3c**) together with 4-benzoyl-4*H*-benzo[*def*]carbazole (**3g**). The corresponding monobenzoyl derivative was not isolated. The results of the Friedel-Crafts reaction suggest that the para-position to the nitrogen atom in **1c** has higher electron density than those to the methylene group or the oxygen atom in **1a** and **1b**.

The hydrogenation of **1a**, **1b**, and **1c** in the presence of palladium–charcoal gave the corresponding 8,9-dihydro derivatives, **4a**, **4b**, and **4c**, respectively. The double bond at the 9,10-positions of phenanthrene were not hydrogenated under the reaction conditions. Gas chromatographic analysis showed that the rate of reduction from pyrene to 4,5-dihydropyrene was comparable to that of the double bond at the 8,9-positions in **1a** but the rate from 4,5-dihydropyrene to 4,5,9,10-tetrahydropyrene was very slow. This suggests that facile hydrogenation of **1a**, **1b**, and **1c** to the corresponding 8,9-dihydro derivatives (**4a**, **4b**, and **4c**) are due to strain in the fused ring system of **1a**—**c**. This explanation is supported by the fact that reduction of **1b** with lithium aluminium hydride afforded 4-phenanthrol.[1]

The reduction of **1a** with sodium–ethanol gave **4a**, and the reduction of **1b** afforded 3,3a,8,9,9a,9b-hexahydrophenanthro[4,5-*bcd*]furan (**5b**). In the case of **1c**, two products, **4c** and 3,8,9,9a-tetrahydro-4*H*-benzo[*def*]-carbazole (**5c**), were obtained in 44% and 29% yields, respectively. Thus, not only the double bonds at the 8,9-positions but also the benzene rings which have hetero-atom substituents were readily reduced when the bridge linkage of X was a hetero-atom. The double bond at the 9,10-positions in phenanthrene was however not reduced under the reaction conditions. Thus, the double bonds at the 8,9-positions in **1a**, **1b**, and **1c** were readily reduced with sodium–ethanol and by catalytic hydrogenation.

## Experimental

*4H-Cyclopenta*[def]*phenanthrene (**1a**).* Colorless plates from methanol; mp 113.5—114.5 °C (lit,[4] 114—115 °C). IR (KBr): $\nu_{max}$ 754, 817 cm$^{-1}$ (Ar–H). $^1$H NMR ($CDCl_3$): $\delta$ 4.22 (2H, s, $-CH_2-$), 7.45—7.78 (6H, m, Ar–H), 7.73 (2H, s, Ar–H). $^{13}$C NMR ($CDCl_3$): $\delta$ 37.1 (C-4), 120.9 (C-3), 122.4, 125.1, 127.0, 127.9 (C-9), 138.2 (C-9b), 141.6 (C-3a). UV(EtOH): $\lambda_{max}$ ($\varepsilon$) 210 (24300), 220$^{sh}$ (26600), 222 (27800), 225 (24700), 249$^{sh}$ (47500), 252 (50700), 261 (18400), 275 (8700), 287 (10600), 299 nm (12800).

*4H-Benzo*[def]*carbazole (**1c**).* Colorless plates from benzene–hexane; mp 172—173 °C (lit,[3a] 170—173 °C). IR (KBr): $\nu_{max}$ 750, 820 (Ar–H), 3445 cm$^{-1}$ (NH). $^1$H NMR ($CDCl_3$): $\delta$ 7.25 (2H, dd, $J$=3 and 6 Hz, Ar–H), 7.62—7.80 (5H, m, Ar–H+NH), 7.94 (2H, s, Ar–H). $^{13}$C NMR ($CDCl_3$): $\delta$ 106.0 (C-3), 115.3, 122.3 (C-9b), 126.0, 126.8, 127.4 (C-9a), 138.8 (C-3a). UV(EtOH): $\lambda_{max}$ ($\varepsilon$) 234 (63100), 273 (17600), 283 (13500), 332 (12200), 346 nm (10900).

*1,3,5,7-Tetrabromo-4H-benzo*[def]*carbazole (**2c**).* Bromine (1.1 g) in carbon tetrachloride (20 ml) was added to a carbon tetrachloride solution (30 ml) of **1c** (300 mg), and the mixture stirred for 1 h at room temperature. The precipitated crystals were collected by filtration to give 660 mg (83%) of **2c**. Recrystallization from tetrahydrofuran–benzene gave colorless needles; mp 294—295 °C (lit,[3b] mp 292—293 °C). IR (KBr): $\nu_{max}$ 808 (Ar–H), 3460 cm$^{-1}$ (NH). UV(EtOH): $\lambda_{max}$ ($\varepsilon$) 242 (45800), 248 (50000), 272 (18300), 288 (19000), 298 (13600), 353 (19100), 372 nm (21200). Found: C, 33.25; H, 1.14; N, 2.85%. Calcd for $C_{14}H_5NBr_4$: C, 33.18; H, 0.99; N, 2.76%.

*8-Bromo-4H-cyclopenta*[def]*phenanthrene (**2a**) and 4-Bromo-4H-cyclopenta*[def]*phenanthrene (**2e**).* Bromine (540 mg) in carbon tetrachloride (10 ml) was added to a carbon tetrachloride solution (30 ml) of **1a** (600 mg), and the solution stirred for 1 h at room temperature. After removal of the solvent, the resulting oil was chromatographed on silica gel and eluted with benzene–hexane (1:9). The first fraction gave 370 mg (42%) of **2a**. Recrystallization from methanol gave colorless needles; mp 91—92 °C. IR(KBr): $\nu_{max}$ 770, 780 cm$^{-1}$ (Ar–H). NMR ($CDCl_3$): $\delta$ 4.13 (2H, s, Ar–$CH_2$–), 7.42—7.90 (6H, m, Ar–H), 7.96 (1H, s, Ar–H). UV (EtOH): $\lambda_{max}$ ($\varepsilon$) 206 (26900), 223 (33900), 251 (48800), 257 (44400), 267 (22000), 283 (9600), 295 (14000), 308 nm (15500). Found: C, 66.73; H, 3.40%. Calcd for $C_{15}H_9Br$: C, 66.94; H, 3.37%.

The second fraction afforded 260 mg (30%) of **2e**. Recrystallization from methanol gave colorless needles; mp 131—132 °C. IR(KBr): $\nu_{max}$ 825 cm$^{-1}$ (Ar–H). NMR ($CDCl_3$): $\delta$ 6.30 (1H, s, Ar–CHBr), 7.50—7.80 (8H, m, Ar–H). UV (EtOH): $\lambda_{max}$ ($\varepsilon$) 227 (56700), 243 (21900), 257 (20700), 285 (13600), 298 nm (11700). Found: C, 66.89; H, 3.65%. Calcd for $C_{15}H_9Br$: C, 66.94; H, 3.37%.

*Bromination of **1a** with* N-*Bromosuccinimide.* *N*-Bromosuccinimide (600 mg) was added to a carbon tetrachloride solution (10 ml) of **1a** (300 mg) and the mixture refluxed for 2 h. After removal of insoluble materials by filtration the solvent was evaporated. The resulting crystals were chromatographed on silica gel and eluted with benzene–hexane (1:9) to give 320 mg (73%) of **2e**. The compound was identical with the product obtained by the bromination of **1a** with bromine.

*1,7-Dibenzoyl-4H-benzo*[def]*carbazole (**3c**) and 4-Benzoyl-4H-benzo*[def]*carbazole (**3g**).* Anhydrous aluminium chloride (840 mg) was added to a carbon disulfide solution (16 ml) of **1c** (400 mg) and benzoyl chloride (800 mg). The mixture was stirred for 6 h at room temperature, decomposed with dilute hydrochloric acid, and extracted with tetrahydrofuran. The solution was washed with water, dried, and evaporated. The resulting crystals were divided into a benzene-insoluble portion and a benzene-soluble portion. The benzene-insoluble portion (270 mg; 32%) was recrystallized from tetrahydrofuran–benzene to give **3c** as yellow needles; mp>300 °C. IR (KBr): $\nu_{max}$ 820 (Ar–H), 1630 (Ar–CO), 3240 cm$^{-1}$ (NH). UV (EtOH): $\lambda_{max}$ ($\varepsilon$) 210 (31200), 237 (41200), 258 (43500), 296 (23000), 397 nm (33500). Found: C, 84.36; H, 4.43; N, 3.55%. Calcd for $C_{28}H_{17}O_2N$: C, 84.19; H, 4.29; N, 3.51%.

The benzene-soluble portion was chromatographed on silica gel and eluted with benzene. The first fraction gave 100 mg (25%) of the starting material (**1c**), and the second fraction afforded 90 mg (15%) of **3g**. Recrystallization from ethanol

gave colorless needles; mp 141—142 °C (lit,[3a] 141—142 °C). IR (KBr): $\nu_{max}$ 825 (A-H), 1660 $cm^{-1}$ (Ar-CON). NMR ($CDCl_3$): $\delta$ 7.36—7.77 (11H, m, Ar-H), 7.84 (2H, s, Ar-H). UV (EtOH): $\lambda_{max}$ ($\varepsilon$) 213 (42800), 227 (43000), 256 (30600), 303 (15500), 315[sh] (13900), 338 (2800), 345 (1500), 354 nm (2000). Found: C, 85.50; H, 4.61; N, 4.60%. Calcd for $C_{21}H_{13}ON$: C, 85.40; H, 4.44; N, 4.74%.

*1-Benzoyl-4H-cyclopenta*[def]*phenanthrene (3a).* Anhydrous aluminium chloride (300 mg) was added to a carbon disulfide solution of **1a** (300 mg) and benzoyl chloride (330 mg). The mixture was 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 evaporated. The resulting oil was chromatographed on silica gel and eluted with benzene–hexane (4: 1) to give 380 mg (82%) of **3a**. Recrystallization from methanol gave colorless needles; mp 129—130 °C. IR (KBr): $\nu_{max}$ 1640 $cm^{-1}$ (Ar-CO). NMR ($CDCl_3$): $\delta$ 4.29 (2H, s, Ar-$CH_2$), 7.32—7.90 (7H, m, Ar-H), 8.23 (1H, d, $J$=9 Hz, Ar-H). UV (EtOH): $\lambda_{max}$ ($\varepsilon$) 210 (34200), 225 (29200), 252 (51200), 321 nm (9600). Found: C, 89.54; H, 4.92%. Calcd for $C_{22}H_{14}O$: C, 89.77; H, 4.79%.

*8,9-Dihydro-4H-benzo*[def]*carbazole (4c).* A mixture of **1c** (400 mg), 8% palladium–charcoal (350 mg), and ethanol (30 ml) was shaken for 20 h at room temperature under a hydrogen atmosphere. After removal of the catalyst by filtration, the ethanol was evaporated under reduced pressure. The resulting crystals were chromatographed on silica gel and eluted with benzene–hexane (1: 1) to give 330 mg (82%) of **4c**. Recrystallization from benzene–hexane gave colorless plates; mp 124—125 °C (lit,[3b] 124—125 °C). IR (KBr): $\nu_{max}$ 773 (Ar-H), 3430 $cm^{-1}$ (NH). NMR ($CDCl_3$): $\delta$ 3.27 (4H, s, $-CH_2-+-CH_2-$), 6.93 (2H, d, $J$=8 Hz, Ar-H), 7.01 (2H, d, $J$=8 Hz, Ar-H), 7.26 (2H, t, $J$=8 Hz, Ar-H), 7.39 (1H, broad s, NH). UV (EtOH): $\lambda_{max}$ ($\varepsilon$) 216 (40300), 246 (34500), 255 (24000), 294 (12000), 316 (3600), 329 nm (3000). Found: C, 86.82; H, 5.83; N, 7.01%. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25%.

*8,9-Dihydro-4H-cyclopenta*[def]*phenanthrene (4a).* Hydrogenation of **1a** to **4a** (89% yield) was conducted by the method employed for reduction of **1c**. Recrystallization from methanol gave colorless plates; mp 139—140 °C (lit,[3a] 138—140 °C). IR (KBr): $\nu_{max}$ 765 $cm^{-1}$ (Ar-H). NMR ($CDCl_3$): $\delta$ 3.10 (4H, s, Ar-$CH_2$+Ar-$CH_2$), 3.83 (2H, s, Ar-$CH_2$), 6.99—7.34 (6H, m, Ar-H). UV (EtOH): $\lambda_{max}$ ($\varepsilon$) 214 (37000), 228 (15100), 273 (18000), 282 nm (14000). Found: C, 93.47; H, 6.40%. Calcd for $C_{15}H_{12}$: C, 93.71; H, 6.29%.

*Reduction of 1c with Sodium and Ethanol.* An ethanolic solution (20 ml) of **1c** (200 mg) was heated under reflux. To the solution sodium (3.7 g) was added in limited amounts. When precipitates of sodium ethoxide were produced, additional ethanol (20 ml) was introduced into the solution and the residual sodium was added. After the sodium had disappeared (1 h), the mixture was poured into ice water, and extracted with ether. The ethereal layer was washed with water, dried, and evaporated. The resulting oil was chromatographed on silica gel and eluted with benzene–hexane (1: 1). The first fraction gave 90 mg (44%) of **4c**. The product was identical with the product obtained by the catalytic hydrogenation of **1c** in melting points and infrared spectra. The second fraction afforded 60 mg (29%) of **5c** as crystals. Recrystallization from benzene–hexane gave colorless needles; mp 127—128 °C (lit,[3a] 125—126 °C). IR (KBr): $\nu_{max}$ 3420 $cm^{-1}$ (NH). NMR ($CDCl_3$): $\delta$ 1.13—1.53 (1H, m, $-CH_2-$), 2.12—2.35 (1H, m, $-CH_2-$), 2.70—3.32 (4H, m, $-CH_2-+-CH_2-$), 3.37—3.53 (1H, m, Ar-CH=), 5.72—6.01 (2H, m, -CH=CH-), 6.72—7.31 (4H, m, Ar-H+NH). UV (EtOH): $\lambda_{max}$ ($\varepsilon$) 230 (31900), 283 nm (5800). Found: C, 86.25; H, 6.73; N, 7.41%. Calcd for $C_{11}H_{13}N$: C, 86.11; H, 6.71; N, 7.17%.

*Reduction of 1a with Sodium and Ethanol.* **1a** was reduced by a method similar to the hydrogenation of **1c** with sodium and ethanol. The resulting oil was chromatographed on silica gel and eluted with benzene–hexane (1: 9) to give 130 mg (65%) of **4a**. The product was identical with the sample obtained by the catalytic hydrogenation of **1a** with palladium–charcoal in melting points and infrared spectra.

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