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Regioselectivity in the Controversial Scholl Reaction of 1-Benzoylpyrene: Formation of a Five-Member Ring Is Not Unexpected

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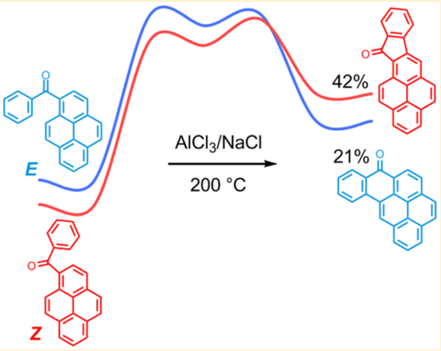
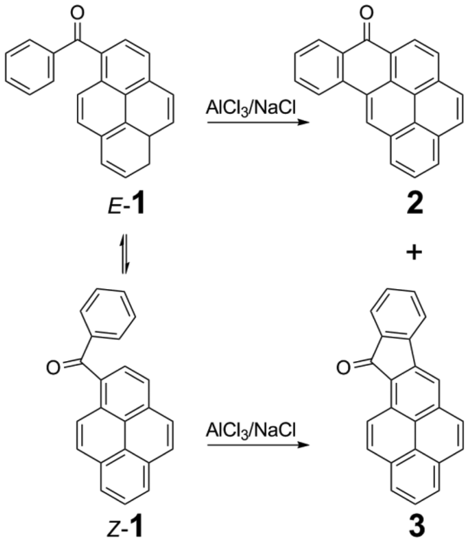
Ⓢ *Supporting Information*

ABSTRACT: Intramolecular Scholl reaction of 1-benzoylpyrene (**1**) gave 8*H*-dibenzo[*def*,*qr*]chrysen-8-one (**2**) and 11*H*-indeno[2,1-*a*]pyren-11-one (**3**) in a 1:2 ratio. The structures of **2** and **3** were determined, using ^{1}H NMR, ^{13}C NMR, and IR spectroscopies. A DFT B3LYP/6-311G(d,p) study of the reaction's arenium−cation mechanism of (*E*)-**1** and (*Z*)-**1** giving **2** and **3**, respectively, indicated the reaction's regioselectivity and kinetic control. The analogous reaction of 1-(1′-naphthoyl)pyrene gave exclusively 13*H*-benz[4,5]indeno[2,1-*a*]pyren-13-one. Contrary to previous claims, the preferred formation of five-member rings in Scholl reactions is not unexpected.



The century-old Scholl reaction[1,2] has recently undergone a renaissance. A controversial important issue in its study is the preferred formation of a six-member ring versus a five-member ring by dehydrogenative aromatic C⋯C coupling.[2] "The Scholl reactions leading to the formation of six-member rings are by far the most numerous."[3] In 1966, it was reported that contrary to Vollmann's 1937 seminal pyrene article,[4] the major product (mp 242 °C) of the Scholl reaction of 1-benzoylpyrene (**1**) ($AlCl_3$/NaCl melt) was not the $C_6C_6C_6C_6$-C_6C_6 8*H*-dibenzo[*def*,*qr*]chrysen-8-one (**2**), but the $C_5C_6C_6$-$C_6C_6C_6$ 11*H*-indeno[2,1-*a*]pyren-11-one (**3**) (Scheme 1 and Figure S1).[5] The authors also isolated isomeric **2**.[5] However, the structures of **2** and **3** were based solely on their infrared carbonyl absorptions, ν = 1695 cm^{-1} in **3** (characteristic of 9-fluorenones) and ν = 1642 cm^{-1} in **2**.[5] This hardly substantiated communication has since been mostly overlooked, whereas Vollmann's original work[4] has been followed.[6−8] Morgenthaler and Ruechard reported that **1** has been cyclized in an $AlCl_3$/NaCl melt to afford **2** in low yield: orange-colored needles, mp 245−248 °C (lit.[4] mp 242 °C), IR ν = 1697 cm^{-1} (C═O).[6] Preda and Scott reported that **2** (mp 214−216 °C) was formed by FVP of 1-(2-bromobenzoyl)-pyrene at 1100 °C, also referring to Vollmann's mp of 242 °C for **2**.[7] Both reports provided ^{1}H NMR spectra of their products.[6,7] Clar also referred to the alleged Scholl reaction product **2**,[8] whereas **3** was only briefly mentioned as an environmental sample.[9]

Scheme 1. Intramolecular Scholl Reaction of 1-Benzoylpyrene (1)



Balaban and Nenitzescu reformulated the Scholl reaction as "the elimination of two aryl-bound hydrogens accompanied by the formation of an aryl−aryl bond under the influence of a Friedel−Crafts catalyst".[3] The Scholl reaction has been reviewed[3,10,11] and extensively applied to the synthesis of polycyclic aromatic hydrocarbons (PAHs) and ketones (PAKs), including large PAHs.[12] The claimed intramolecular Scholl reaction of **1** leading to **2** (minor) and **3** (major)[5] involves the formation of a six-member ring and a five-member ring, respectively. Very recently, an unexpected selective formation

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of five-member rings in PAHs in a Scholl reaction has been highlighted.[13]

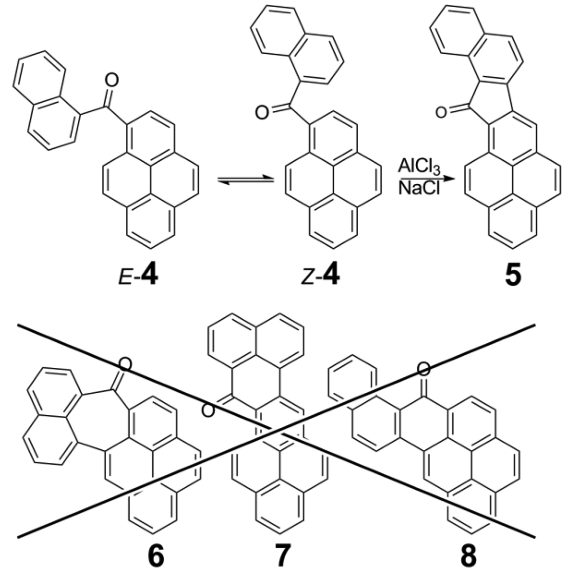
We report here conclusive evidence of the structures of products **2** and **3**, formed in the Scholl reaction of **1** [a mixture of (*E*)-**1** and (*Z*)-**1**] in a 1:2 ratio. We note that the reaction is regioselective: the major product **3** is formed from (*Z*)-**1**, whereas the minor product **2** is formed from (*E*)-**1** (Scheme 1). A mechanism based on a DFT study shows that this Scholl reaction is kinetically controlled and not thermodynamically controlled.

Intramolecular Scholl Reactions of Acylpyrenes. Treatment of 1-benzoylpyrene (**1**)[4] with an $AlCl_3$/NaCl melt (2.9:1) at 140 °C (30 m) and then at 200 °C (1 h) in an Ar atmosphere gave after workup a crude mixture of **2** and **3** in a 1:2 ratio. Column chromatography on silica gel gave pure **2** (mp 242−244 °C) and pure **3** (mp 235−237 °C) in 21 and 42% yields, respectively. The structures of **2** and **3** were verified by elemental analysis and ^{1}H NMR and ^{13}C NMR spectra (complete assignments), including two-dimensional (2D) correlation spectroscopy (COSY, HSQC, HMBC, and ROESY), IR carbonyl absorptions, and mass spectra. The IR carbonyl absorptions [ν = 1642 cm^{-1} (**2**) and 1691 cm^{-1} (**3**)] and the ^{13}C NMR chemical shifts of the carbonyl groups [δ = 183.8 ppm (**2**) and 194.9 ppm (**3**)] resemble those of 7*H*-benz[*de*]anthracen-7-one[14] [ν = 1644 cm^{-1}, δ(C═O) = 183.9 ppm (183.8 ppm[15])] and 11*H*-benzo[*a*]fluoren-11-one[16] [ν = 1695[17] cm^{-1}, δ(C═O) = 195.4 ppm[17]], respectively. The Scholl reaction of **1** is not reversible: treatment of either **2** or **3** under the same experimental conditions has afforded only the respective starting material. Running the reaction over the temperature range of 160−260 °C for 1 h or prolonging the reaction time to 2 and 4 h (at either 180 or 260 °C) yielded **2** and **3** in a constant 1:2 ratio. At 160 °C, the yield of the reaction is only 5% of **2** and **3** combined.

The ^{1}H and ^{13}C NMR chemical shifts of **2** and **3** (see Experimental Section) are depicted in Figure S23. The very low field signals of H^{13} [δ = 9.14 ppm (s)] and H^{7} [δ = 9.11 ppm (d)] in **2** and of H^{12} [δ = 9.24 ppm (d)] in **3** are noted. Strikingly, the ^{1}H ROESY through-space correlations in the overcrowded regions, $H^{13}\cdots H^{1}$ and $H^{13}\cdots H^{12}$ in **2** and $H^{6}\cdots H^{5}$ and $H^{6}\cdots H^{7}$ in **3**, have been revealed. The resemblance in the ^{1}H NMR chemical shifts (of the hydrogens at the distal benzannelated ring) between **2** and 7*H*-benz[*de*]anthracen-7-one and between **3** and 11*H*-benzo[*a*]fluoren-11-one is also evident. The UV/vis spectra of **2** and **3** also differ.

The intramolecular Scholl reaction of 1-(1′-naphthoyl)-pyrene (**4**)[18] ($AlCl_3$/NaCl, 200 °C, 1 h, Ar) gave exclusively the five-member ring $C_5C_6C_6C_6C_6C_6C_6$ PAK 13*H*-benz[4,5]-indeno[2,1-*a*]pyren-13-one [**5** (Figure S1)], mp 315 °C, in 49% yield. It is necessarily formed from the (1*Z*,1′*Z*)-**4** conformer by $C^{2}\cdots C^{2'}$ *ortho*−*ortho* coupling (Scheme 2). Conformers (1*E*,1′*E*)-**4**, (1*Z*,1′*E*)-**4**, and (1*E*,1′*Z*-)**4** would have led by $C^{10}\cdots C^{8'}$ *peri*−*peri*′, $C^{2}\cdots C^{8'}$ *ortho*−*peri*, and $C^{10}\cdots C^{2'}$ *peri*−*ortho* couplings to the constitutional isomeric $C_6C_6C_6C_6C_6C_6C_7$, $C_6C_6C_6C_6C_6C_6C_6$, and $C_6C_6C_6C_6C_6C_6C_6$ PAKs **6**−**8**, respectively. The structure of **5** was determined by elemental analysis and IR, mass, and ^{1}H NMR and ^{13}C NMR spectroscopies, including 2D experiments. In particular, the IR carbonyl absorption (ν = 1682 cm^{-1}, characteristic of fluorenones[17]) confirms the structure of **5**. The absence of long-range H⋯C═O interactions in the HMBC experiment rules out the isomeric PAKs **6**−**8** as reaction products. **5** is the only product of the Scholl reaction of **4**. Experiments conducted at various temperatures (180−260 °C for 1 h) and for various reaction times (1, 2, and 4 h at either 180 or 260 °C) gave exclusively **5**. DFT calculations provide a plausible explanation for these results (*vide infra*).

Scheme 2. Intramolecular Scholl Reaction of 1-(1′-Naphthoyl)pyrene (4)

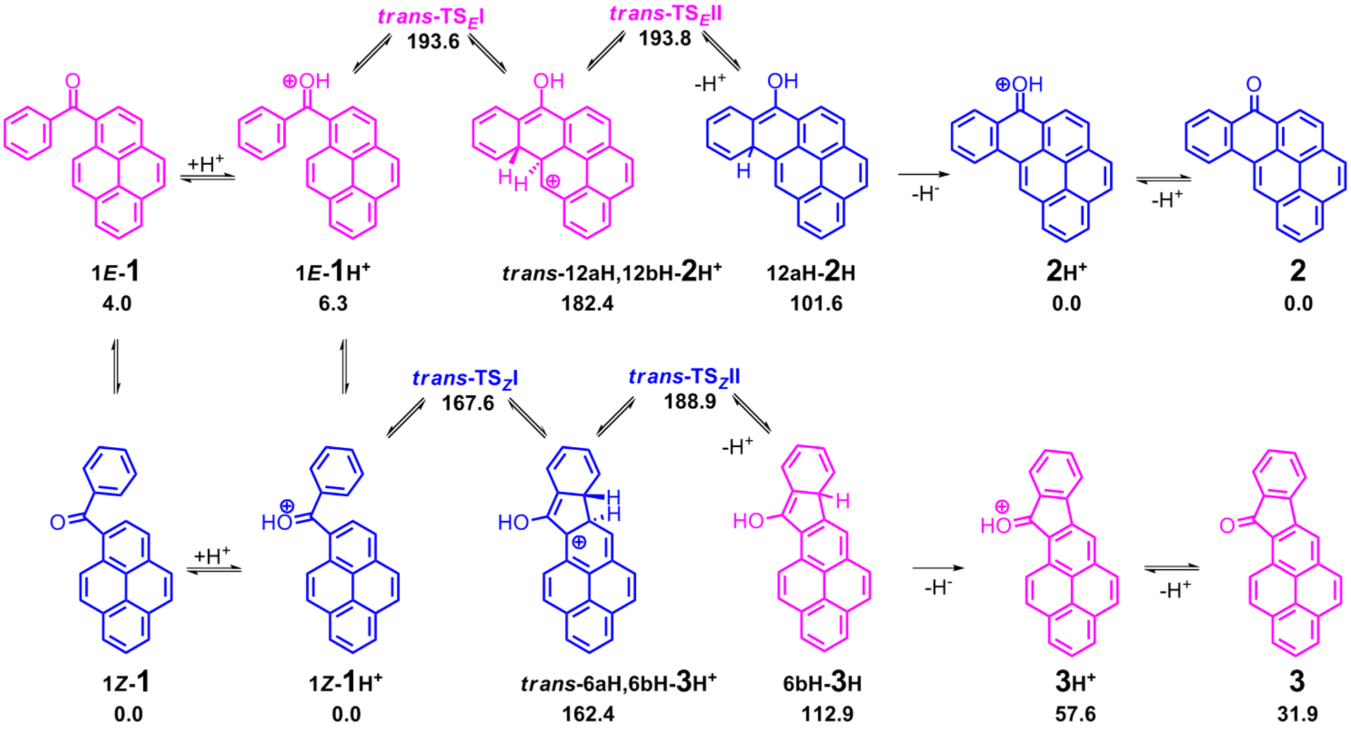


DFT Study of the Scholl Reaction Mechanism. DFT B3LYP/6-311G(d,p) calculations, including solvent effects (see the Supporting Information for details), have been employed to explore the mechanism of the intramolecular Scholl reaction of **1** leading to **3** and **2**.[19] For the Scholl reaction, arenium-cation (proton transfer)-based and radical-cation (electron transfer)-based mechanisms have been proposed.[3,10,20] Previous quantum mechanical calculations demonstrated that the arenium-cation mechanism proceeds via a lower energetic barrier and therefore is energetically favored over the radical-cation mechanism.[21,22] In the work presented here, only the arenium-cation-based mechanism has been studied.

The mechanism of the Scholl reaction of **1** is presented in Scheme 3 (see Scheme S1 for details). For the purposes of the quantum mechanical calculations, H^{+} was used as a model for a Lewis acid (e.g., $AlCl_3$). The starting PAK **1** exists as a mixture of (*Z*) and (*E*) diastereomers/conformers[23] with an equilibrium distribution of 83% (*Z*) and 17% (*E*) {benzoyl torsion angles $O-C^{11}-C^{1}-C^{10a}$ ω = 40° [(*Z*)-**1**] and 126° [(*E*)-**1**]; ΔG_{298} = 4.0 kJ/mol}. The reaction begins with converting **1*E*-1** and **1*Z*-1** into O-protonates **1*Z*-1H**$^{+}$ and **1*E*-1H**$^{+}$, respectively, also existing in a rapid thermal $E \rightleftharpoons Z$ equilibrium, with an equilibrium distribution of 93% (*E*) and 7% (*Z*) [ω = 23° (*Z*) and 152° (*E*); ΔG_{298} = 6.3 kJ/mol]. In the second step, **1-1H**$^{+}$ undergoes an intramolecular electrophilic substitution. Because of geometry constraints, the *peri*−*ortho* cyclization of **1*E*-1H**$^{+}$ involves the formation of a six-member ring, leading to the σ-complex *trans*-**12aH,12bH-2H**$^{+}$ via transition state *trans*-$\mathbf{TS_{E}I}$. On the other hand, the *ortho*−*ortho* cyclization of **1*Z*-1H**$^{+}$ involves the formation of a five-member ring, giving *trans*-**6aH,6bH-3H**$^{+}$ via transition state *trans*-$\mathbf{TS_{Z}I}$. The free energy barriers ($\Delta\Delta G^{\ddagger}$) for these cyclizations are 187.3 (=193.6 − 6.3) and 167.6 kJ/mol, respectively.

An alternative mechanism of the formation of the σ-complex *trans*-**6aH,6bH-3H**$^{+}$ is the Nazarov cyclization,[24−26] an acid-

Scheme 3. Mechanism of the Scholl Reaction of 1[a]



[a] B3LYP/6-311G(d,p) PCM calculations. The ΔG_{298} values are in kilojoules per mole. Only *trans* diastereomers are shown.

catalyzed closure of divinyl ketones to 2-cyclopentenones. Mechanistically, the determining step of the Nazarov cyclization is a concerted 4*π*-electrocyclization. The thermal concerted pathway is conrotatory, leading to a *trans* diastereomer intermediate. Thus, **1*Z*-1H**$^+$ → [*trans*-**TS$_Z$I**]$^\#$ → *trans*-**6aH,6bH-3H**$^+$. The latter diastereomeric *σ*-complex is 24.3 kJ/mol lower in energy than *cis*-**6aH,6bH-3H**$^+$. By contrast, the thermal concerted 6*π*-electrocyclic hexatriene−cyclohexadiene reaction of **1*E*-1H**$^+$ is disrotatory and would lead to a *cis* diastereomer: **1*E*-1H**$^+$ → [*cis*-**TS$_E$I**]$^\#$ → *cis*-**12aH,12bH-2H**$^+$. The latter is 25.3 kJ/mol higher in energy than *trans*-**12aH,12bH-2H**$^+$. The energies of transition states *trans*-**TS$_Z$I** and *trans*-**TS$_E$I** are 147.9 and 48.5 kJ/mol lower than those of *cis*-**TS$_Z$I** and *cis*-**TS$_E$I**, respectively. The $\Delta G_{trans} - \Delta G_{cis}$ differences of the *σ*-complexes and of the respective transition states support the Nazarov-like 4*π*-electrocyclization mechanism in the case of the **1*Z*-1** → **3** pathway and rule out the 6*π*-electrocyclization mechanism in the case of the **1*E*-1** → **2** pathway. Furthermore, these differences explain the preferred formation **5** versus **6−8**.

In the next step, the *σ*-complexes *trans*-**12aH,12bH-2H**$^+$ and *trans*-**6aH,6bH-3H**$^+$ undergo deprotonation with the partial rearomatization of their newly formed six- and five-member rings, via the respective highest transition states *trans*-**TS$_E$II** and *trans*-**TS$_Z$II**, giving **12aH-2H** and **6bH-3H**, respectively. The free energy barriers for these deprotonation steps are 11.4 and 26.5 kJ/mol, respectively. The enol forms **12aH-2H** and **6bH-3H**, presented in Scheme 3, exist in equilibrium with their respective keto tautomers (not shown). Hydride loss from **12aH-2H** and **6bH-3H** leads to the respective O-protonated ketones **2H**$^+$ and **3H**$^+$, which are deprotonated to give **2** and **3**, respectively. The last steps in the mechanism of the Scholl reaction of **1** (Scheme 3) involve an oxidative dehydrogenation (loss of a hydride and a proton is shown). A possible oxidant is $AlCl_3$, which has been reported to possess powerful dehydrogenation action.[3,27,28] The carbonyl group (present in **1** and in many Scholl reaction precursors) can also serve as a temporary oxidizing agent.[3,10] Oxidizing agents such as air and oxygen have also been used.[28] However, the Scholl reactions of **1** and of **4** were conducted under an inert (Ar) atmosphere. It was noted that "what is missing especially in the case of the $AlCl_3$ solvent systems is a measure of their oxidizing or hydride ion abstracting power".[28]

We note that (*E*) diastereomers/(*E*) conformers **1*E*-1**, **1*E*-1H**$^+$, and *trans*-**12aH,12bH-2H**$^+$, as well as transition states *trans*-**TS$_E$I** and *trans*-**TS$_E$II**, are invariably higher in energy than the respective (*Z*) diastereomers/(*Z*) conformers and derivatives of **3**. By contrast, **12aH-2H**, **2H**$^+$, and **2** are lower in energy than their constitutional isomers **6bH-3H**, **3H**$^+$, and **3**, respectively, partially because of the presence of an antiaromatic five-member ring in the latter.[29,30] The switch in the relative stabilities occurs in the partial rearomatization steps *trans*-**12aH,12bH-2H**$^+$ → **12aH-2H** and *trans*-**6aH,6bH-3H**$^+$ → **6bH-3H** (Scheme 3). *trans*-**12aH,12bH-2H**$^+$ is higher in energy than *trans*-**6aH,6bH-3H**$^+$ ($\Delta\Delta G_{298}$ = 20.0 kJ/mol), and the respective *trans*-**TS$_E$II** is higher in energy than *trans*-**TS$_Z$II** ($\Delta\Delta G_{298}$ = 4.9 kJ/mol); on the other hand, **12aH-2H** is lower in energy than **6bH-3H** ($\Delta\Delta G_{298}$ = 11.3 kJ/mol). The lower relative free energies of *trans*-**6aH,6bH-3H**$^+$ and of *trans*-**TS$_Z$II** are considered to be the determining factors in the reaction outcome. Both formal overall reactions, **1** → **2** + H_2 and **1** → **3** + H_2 are exothermic, with ΔG_{298} values of −47.3 and −12.1 kJ/mol, respectively [at B3LYP/6-311G(d,p)]. The experimental results show that the less stable isomer, **3**, is the major product whereas the more stable isomer, **2**, is the minor product. Thus, the Scholl reaction of **1** is kinetically controlled.

The DFT calculations of PAKs **5−8** and their derivatives (Table S5) show that **8** is the most stable constitutional isomer

(ΔG_{298} = 0.0 kJ/mol), compared with **7** (9.3 kJ/mol), **5** (23.0 kJ/mol), and **6** (95.4 kJ/mol). The order of stabilities of the respective protonates is identical. However, the protonated 6aH,6bH-σ complex of **5** (Scheme S4) has the lowest energy compared with those of its constitutional isomers; the energies of the respective σ-complexes of **8** and **7** are higher ($\Delta\Delta G_{298}$ = 19.8 and 58.7 kJ/mol, respectively). According to the Hammond–Leffler postulate,[31] the relative energies of the transition states leading to the σ-complexes resemble those of the σ-complexes. Thus, the energy barrier for the **4** → **5** pathway is the lowest among those of isomeric products **5**–**8**, which may explain the exclusive formation of **5** in the Scholl reaction of **4**.

In conclusion, the intramolecular Scholl reaction of **1** is regioselective. Mechanistically, because of geometrical constraints, the less stable, major five-member ring PAK product **3** is formed from the more stable (Z) diastereomer/(Z) conformer of **1**, whereas the more stable, minor six-member PAK product **2** is formed from the less stable (E) diastereomer/(E) conformer of **1**. Kinetic control wins over thermodynamic control. Previously reported structures of PAKs formed by intramolecular Scholl [e.g., the dye pyranthrone (Vat Orange G)] reactions should be verified and/or ruled out. The preferred formation of a five-member ring in a Scholl reaction is not unexpected.

■ EXPERIMENTAL SECTION

IR spectra were recorded on an FT-IR ATR solid state spectrometer. Mass spectroscopy was performed on a Q-TOF LC/MS analyzer using an electrospray ionization method. UV–vis spectra were recorded on a linear silicon CCD detector spectrometer. ^{1}H and ^{13}C NMR spectra were recorded at 500.20 MHz, using chloroform-d (99.8% D, contains 0.03% TMS) as a solvent and internal standard. Column chromatography was performed on silica gel (0.063–0.200 mm).

Scholl Reaction of 1-Benzoylpyrene (1) and Syntheses of 8*H*-Dibenzo[*def*,*qr*]chrysen-8-one (2) and 11*H*-Indeno[2,1-*a*]pyren-11-one (3). The Scholl reaction of **1** was performed according to the method described in the literature[4] with certain modifications. The reaction was conducted in a 100 mL three-neck flask equipped with a mechanical stirrer, a reflux condenser, and a thermometer, under an argon atmosphere. Anhydrous $AlCl_3$ (33.28 g, 250 mmol) and anhydrous NaCl (5.08 g, 87 mmol) were placed in the flask, and the mixture was heated to 140 °C for 30 min to form a melt. Benzoylpyrene (**1**) (4.00 g, 13 mmol) was added in portions, and the reaction mixture was gradually heated while being stirred for 30 min to 200 °C and continued to be stirred at 200 °C for 1 h. The reaction melt was then poured into an ice/water mixture (1 L) and stirred overnight. The resulting solid was filtered off to give the crude products (3.25 g). It was then dissolved while being stirred in boiling acetic acid (50 mL). After the mixture had cooled, cold water (10 mL) was added, and the resulting solid was filtered off. The purification in acetic acid was repeated three times to give a mixture of products (3.01 g). Recrystallization of the mixture from acetic acid (50 mL) in the presence of active charcoal gave **2** and **3** (2.82 g) in 71% yield. Column chromatography on silica gel with a gradient elution using petroleum ether (40–60 °C)/CH_2Cl_2 gave two fractions: **2** (0.830 g), mp 242–244 °C (lit.[4] 242 °C), yellow-orange solid, and **3** (1.66 g), mp 235–237 °C, yellow-orange solid (mixed mp 214–216 °C) in 21 and 42% yields, respectively, in a 1:2 ratio. A 0.47:1.00 **2**:**3** ratio of the recrystallized mixture of products was determined on the basis of the ^{1}H NMR low-field doublets at δ = 9.11 ppm (H^7, **2**) and δ = 9.24 ppm (H^{12}, **3**).

8H-Dibenzo[def,qr]chrysen-8-one (**2**). Anal. Calcd for $C_{23}H_{12}O$: C, 90.77; H, 3.97. Found: C, 90.61; H, 3.89%. HRMS (Q-TOF): m/z [M]$^+$ calcd for $C_{23}H_{12}O$ 304.08881, found 304.09021. TLC (silica gel, 7:3 petroleum ether 40–60 °C/CH_2Cl_2): R_f = 0.32. IR: ν = 1642 cm^{-1} (C═O) (lit.[5] 1642 cm^{-1}). ^{1}H NMR ($CDCl_3$): δ 9.14 (s, 1H, H^{13}), 9.11 (d, ^3J = 8.10 Hz, 1H, H^7), 8.64 (ddd, ^3J = 7.81 Hz, ^3J = 1.59 Hz, ^3J = 1.32 Hz, ^4J = 0.55 Hz, ^4J = 0.52 Hz, 1H, H^9), 8.63 (ddd, ^3J = 8.10 Hz, ^3J = 1.32 Hz, ^3J = 1.17 Hz, ^4J = 0.58 Hz, ^4J = 0.51 Hz, ^4J = 0.47 Hz, 1H, H^{12}), 8.46 (dd, ^3J = 7.62 Hz, ^4J = 0.19 Hz, 1H, H^1), 8.39 (dd, ^3J = 8.01 Hz, ^4J = 0.21, ^4J = 0.16 Hz, 1H, H^6), 8.36 (dd, ^3J = 7.34 Hz, ^4J = 0.48 Hz, ^4J = 0.31, 1H, H^3), 8.28 (dd, ^3J = 8.78 Hz, ^4J = 0.20 Hz, 1H, H^4), 8.21 (d, ^3J = 8.93 Hz, ^4J = 0.18 Hz, 1H, H^5), 8.12 (t, ^3J = 7.63 Hz, 1H, H^2), 7.85 (ddd, ^3J = 8.26 Hz, ^3J = 6.84 Hz, ^4J = 1.52 Hz, ^4J = 1.42 Hz, ^4J = 1.01 Hz, 1H, H^{11}), 7.66 (ddd, ^3J = 8.62 Hz, ^3J = 6.97 Hz, ^4J = 1.07 Hz, ^4J = 1.01 Hz, ^4J = 0.86 Hz, 1H, H^{10}) (lit.[6]). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 183.7 (C^8), 135.8 (C^{12a}), 135.5 (C^{5a}), 132.9 (C^{11}), 131.4 (C^{8a}), 130.6 (C^{3a}), 130.1 (C^{13a}), 129.9 (C^4), 128.8 (C^1), 128.6 (C^{10}), 128.5 (C^3), 128.0 (C^9), 127.9 (C^{13d}), 127.7 (C^5), 126.9 (C^2), 126.5 (C^{13}), 126.3 (C^7), 126.1 (C^{12b}), 126.1 (C^6), 125.6 (C^{7a}), 123.9 (C^{13c}), 123.7 (C^{13b}), 123.1 (C^{12}). UV–vis (CH_2Cl_2): λ (nm) [ε (M^{-1} cm^{-1})] 254 (35235), 279 (27927), 304 (19399), 406 (18713), 430 (25986) (lit.[6] 232, 254, 280, 304, 348, 406, 430 nm).

11H-Indeno[2,1-a]pyren-11-one (**3**). Anal. Calcd for $C_{23}H_{12}O$: C, 90.77; H, 3.97. Found: C, 90.73; H, 3.91. HRMS (Q-TOF): m/z [M]$^+$ calcd for $C_{23}H_{12}O$ 304.08881, found 304.08874. TLC (silica gel, 7:3 petroleum ether 40–60 °C/CH_2Cl_2): R_f = 0.64. IR: ν = 1692 cm^{-1} (C═O) (lit.[5] 1695 cm^{-1}). ^{1}H NMR ($CDCl_3$): δ 9.24 (d, ^3J = 9.17 Hz, 1H, H^{12}), 8.21 (d, ^3J = 8.10 Hz, 1H, H^3), 8.19 (d, ^3J = 7.42 Hz, 1H, H^1), 8.17 (d, ^3J = 8.97 Hz, 1H, H^{13}), 8.16 (s, 1H, H6), 8.15 (d, ^3J = 8.19 Hz, 1H, H^4), 8.06 (d, ^3J = 8.91 Hz, 1H, H^5), 7.98 (d, ^3J = 7.63 Hz, 1H, H^2), 7.71 (d, ^3J = 7.36 Hz, 1H, H^7), 7.70 (d, ^3J = 7.31 Hz, 1H, H^{10}), 7.51 (d, ^3J = 7.59 Hz, ^3J = 7.18 Hz, ^3J = 1.06 Hz, ^4J = 0.85 Hz, ^4J = 0.75 Hz, 1H, H^8), 7.32 (d, ^3J = 7.60 Hz, ^3J = 7.28 Hz, ^3J = 1.34 Hz, ^4J = 1.12 Hz, ^4J = 0.96 Hz, 1H, H^9). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 194.9 (C^{11}), 144.4 (C^{6b}), 142.5 (C^{6a}), 136.3 (C^{3a}), 136.3 (C^{10a}), 134.4 (C^8), 131.5 (C^{13}), 131.0 (C^{5a}), 130.6 (C^{13a}), 130.5 (C^4), 130.2 (C^{11b}), 129.4 (C^9), 127.7 (C^5), 127.4 (C^3), 127.2 (C^1), 126.5 (C^2), 125.5 (C^{13c}), 124.8 (C^{13b}), 124.6 (C^{11a}), 124.0 (C^{10}), 123.2 (C^{12}), 120.5 (C^7), 116.3 (C^6). UV–vis (CH_2Cl_2): λ (nm) [ε (M^{-1} cm^{-1})] 272 (38600), 288 (21000), 305 (17300), 331 (19600), 348 (37300), 430 (26569), 452 (22054).

Scholl Reaction of 1-(1′-Naphthoyl)pyrene (4) and Synthesis of 13*H*-Benz[4,5]indeno[2,1-*a*]pyren-13-one (5). The reaction was conducted in a 100 mL three-neck flask equipped with a mechanical stirrer, a reflux condenser, and a thermometer, under argon. Anhydrous $AlCl_3$ (36.00 g, 270 mmol) and anhydrous NaCl (5.49 g, 94 mmol) were placed in the flask, and the mixture was heated to 140 °C while being stirred for 30 min to form a melt. 1-(1′-Naphthoyl)pyrene[18] (5.00 g, 14 mmol) was added in portions, and the reaction mixture was gradually heated while being stirred for 30 min to 200 °C and continued to be stirred at 200 °C for 1 h. The color changed from brown to bordeaux. The reaction melt was then poured into an ice/water mixture (1 L) and stirred overnight. The resulting solid was filtered off to give the crude products (4.65 g). It was then dissolved while being stirred in boiling acetic acid (70 mL) for 6 h. After filtration, ice-cold water (20 mL) was added and the resulting solid was filtered off. The purification in acetic acid was repeated four times to give a crude product (3.78 g). Recrystallization from acetic acid (60 mL) in the presence of active charcoal gave **5** (3.62 g) in 73% yield. Column chromatography with gradient elution using a 7:3 petroleum ether (40–60 °C)/CH_2Cl_2 solvent gave **5** (2.43 g), mp 309 °C, in 49% yield. Recrystallization from $CHCl_3$ gave orange needles. Mp: 314–316 °C. Anal. Calcd for $C_{27}H_{14}O$: C, 91.50; H, 3.98. Found: C, 91.17; H, 3.84. HRMS (Q-TOF): m/z [M]$^+$ calcd for $C_{27}H_{14}O$ 354.1045, found 354.1061; [M + H]$^+$ 355.1133. TLC (silica gel, 7:3 petroleum ether 40–60 °C/CH_2Cl_2): R_f = 0.71. IR: ν = 1682 cm^{-1} (C═O). ^{1}H NMR ($CDCl_3$): δ 9.23 (d, ^3J = 9.21 Hz, 1H, H^{14}), 9.09 (d, ^3J = 8.51 Hz, 1H, H^{12}), 8.18 (d, ^3J = 7.63 Hz, 1H, H^1), 8.15 (d, ^3J = 6.88 Hz, 1H, H^3), 8.14 (d, ^3J = 9.11 Hz, 1H, H^{15}), 8.13 (s, 1H, H^6), 8.13 (d, ^3J = 8.67 Hz, 1H, H^4), 8.06 (d, ^3J = 8.88 Hz, 1H, H^5), 8.00 (d, ^3J = 8.15 Hz, 1H, H^8), 7.95 (d, ^3J = 7.49 Hz, ^3J = 7.64 Hz, ^3J = 7.51 Hz, 1H, H^2), 7.83 (d, ^3J = 8.14 Hz, 1H, H^7), 7.68 (d, ^3J = 8.30 Hz, 1H, H^9), 7.61 (d, ^3J = 8.97 Hz, ^3J = 6.83 Hz, ^3J = 6.74 Hz, ^4J = 1.48 Hz, ^4J = 1.38 Hz, ^4J = 1.12 Hz, ^4J = 1.03 Hz, 1H, H^{11}), 7.44 (d, ^3J = 8.74 Hz, ^3J = 6.67 Hz, ^4J = 1.13 Hz, ^4J = 0.93 Hz, 1H, H^{10}). ^{13}C{^{1}H} NMR

(CDCl$_3$): δ 196.6 (C^{13}), 145.9 (C^{6b}), 142.1 (C^{6a}), 135.9 (C^{5a}), 135.5 (C^{8}), 134.8 (C^{8a}), 131.5 (C^{15}), 131.1 (C^{3a}), 130.7 (C^{15a}), 130.3 (C^{12a}), 130.2 (C^{4}), 130.0 (C^{13a}), 129.4 (C^{11}), 129.0 (C^{12b}), 128.6 (C^{9}), 127.7 (C^{5}), 127.4 (C^{1}), 127.1 (C^{3}), 126.5 (C^{2}), 126.4 (C^{10}), 125.9 (C^{15c}), 125.0 (C^{15b}), 124.8 (C^{13b}), 124.4 (C^{12}), 123.1 (C^{14}), 118.2 (C^{7}), 116.3 (C^{6}). UV−vis (CHCl$_3$): λ (nm) [ε (M^{-1} cm^{-1})] 266 (23922), 322 (26843), 359 (32304), 443 (6453), 464 (6843).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01798.

> ^{1}H NMR, ^{13}C NMR, IR, and UV/vis spectra of **2**, **3**, and **5**; details of the DFT study of the Scholl reaction of **1** and **4**; relative energies, total energies, and coordinates of derivatives of **1**−**3** and **5**−**8**; and calculated ^{1}H and ^{13}C chemical shifts of **2** and **3** (PDF)

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Notes

The authors declare no competing financial interest.

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