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Reactions of (η^6-Arene)tricarbonylchromium Complexes: Hydrogenation, Nitration, and Bromination

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In this study, we explore the reactions of coordinated arenes, e.g., hydrogenation, nitration, and bromination, to prepare compounds which are not accessible from conventional organic synthesis. The reaction products formed from reactions with the coordinated and the uncoordinated arenes are compared. The polycyclic aromatic hydrocarbons (PAHs) employed for this study include phenanthrene, methyl- and acetylphenanthrene, and benz[*a*]anthracene (BA). The tricarbonylchromium group demonstrated various characteristics which influence the reactions in this work, such as an electronic effect to deactivate hydrogenation, a steric effect to exhibit highly positional selective nitration, and a free radical mechanism to direct bromine to attack at the ring coordinated to tricarbonylchromium.

INTRODUCTION

Since 1957, (η^6-arene)tricarbonylchromium complexes have drawn the attention of organic and organometallic chemists.[1-15] Intensive researches in this field are not only because of interest in the coordination chemistry but also on the basis of the utilization of organometallic complexes to synthesize compounds which cannot be obtained directly from conventional organic reactions. The strong electron-withdrawing character of the tricarbonylchromium moiety in (η^6-arene)tricarbonylchromium complexes is able to reverse the nature of the coordinated arenes. In particular, a variety of nucleophilic aromatic substitution reactions can be carried out on the aromatic system with stereospecific reactions on the functional groups which are attached to the aromatic ring.[16-24]

Polycyclic aromatic hydrocarbons (PAHs) and their derivatives are wide-spread as environmental pollutants.[25-27] Some of them demonstrate strong carcinogenic and/or mutagenic activities.[28-36] Syntheses of these compounds for biological and environmental protection studies are highly significant.[37-38] In this work, we take advantage of coordinated arene to study some reactions, such as hydrogenation, nitration, bromination, and alkylation, for preparing compounds which cannot be derived directly from conventional reactions of arenes. In addition, the products from the parallel reactions in the coordinated and the uncoordinated arenes were carried out for comparison.

RESULTS AND DISCUSSION

Preparation of (η^6-arene) tricarbonylchromium complexes

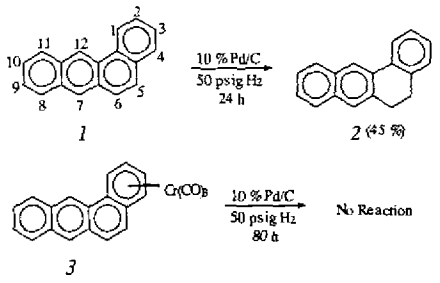
The complexes were prepared from refluxing the solutions of the PAH and chromium hexacarbonyl in the mixture of dibutyl ether and tetrahydrofuran under an atmosphere of nitrogen for a period of 2-4 h depending on the arene used.

In this study, we explore the effect of the presence of a tricarbonylchromium moiety by comparison of the results from the hydrogenation, nitration, bromination, and methylation of PAHs, substituted PAHs, and their (η^6-arene)tricarbonylchromium complexes. Those results are discussed according to the types of reactions (Scheme I, II, III).

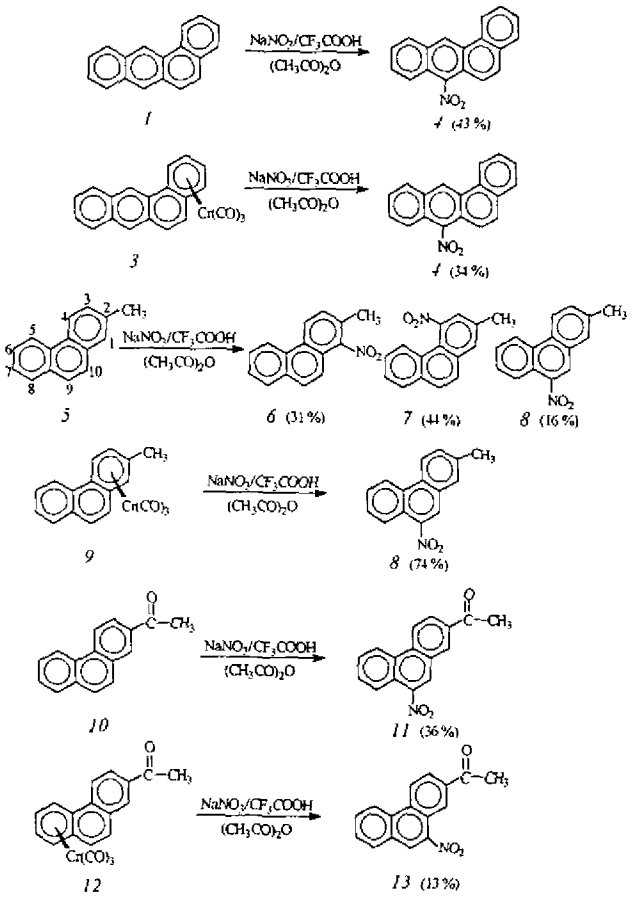
General characteristical comparison of the PAHs, substituted PAHs and their (η^6-arene)tricarbonylchromium complexes

Since an electron-withdrawing character of the tricarbonylchromium moiety is able to change the nature of the coordinated arene towards the reactions, (η^6-arene)tricarbonylchromium complexes have been utilized to synthesize the compounds that cannot be obtained by convenional organic reactions.[1-2] The electron-withdrawing nature of $Cr(CO)_3$ moiety is able to decrease the electron density of the coordinated benzene ring of benz[*a*]anthracene and to increase the proton acidity of that ring resulting in different product distribution from the uncoordinated arene ring.

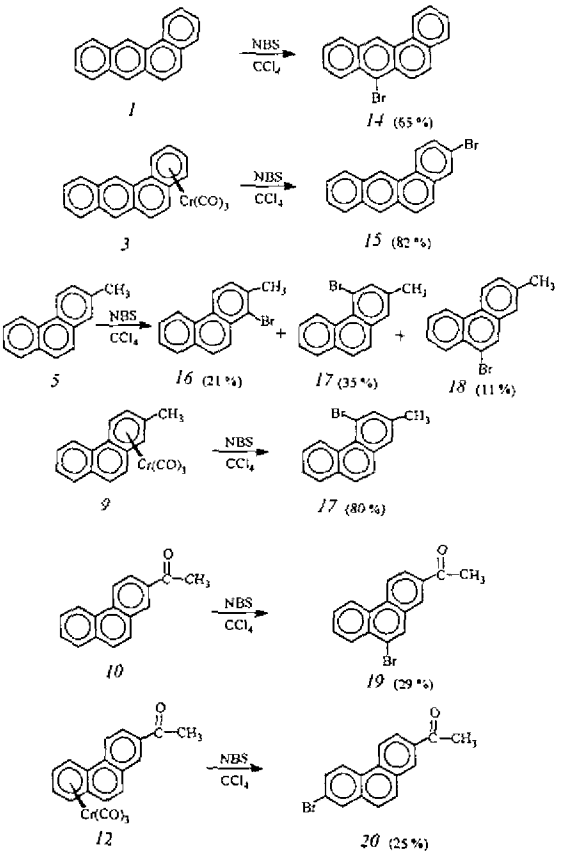
Scheme I Hydrogenation of BA



Scheme II Nitration of PAH **1**, **5**, **10** and coordinated PAH **3**, **9**, **12**



Scheme III Bromination and PAH **1**, **5**, **10** and coordinated PAH **3**, **9**, **12**



Hydrogenation

Benz[*a*]anthracene (**1**) is readily hydrogenated in EA with 10% Pd/C as a catalyst and 50 psig of hydrogen gas for 24 h, the reaction filtrate was purified chromatographically to give a white solid. 5,6-Dihydrobenz[*a*]anthracene (**2**) (45% yield). The results show that the reaction site was at K region (Fig. 2). However, no reaction was observed for (benz[*a*]anthracene)$Cr(CO)_3$ (**3**) even after an 80 h reaction period. This result can be rationalized as: (1) the electron density of the arene in compound **3** was decreased by the $Cr(CO)_3$ moiety resulting in lower electron density on the K region causing it to lose its reactivity. (2) the chromium metal deactivated the catalytic activity of Pd/C due to the bulky moiety (Fig. 2).

Nitration

Sodium nitrate in trifluoroacetic acid was added to a solution of benz[*a*]anthracene (**1**) in acetic acid on an ice bath, after further addition of acetic anhydride, the mixture was stirred at 0 °C for 3 h, the precipitate was collected by filtrating and washing with water. The residue was separated chromatographically over silical gel with EA/hexane (1:20) as an eluent to yield 7-nitrobenz[*a*]anthracene (**4**) (43% yield). Using the same nitration procedure to coordinated compound **3** with a worse yield of 34%. However, presence of the substituent on the PAH leading to the different product distributions is due to variation of electron distribution on the arene system. During nitration of 2-methylphenanthrene (**9**), with an electron-donating methyl group, directs the $Cr(CO)_3$ moiety to bind on the terminal ring of phenanthrene leading more yields on 2-methyl-9-nitrophenanthrene (**11**). In contrast, nitration of compound (**12**) the electron withdrawing 2-acetyl functional group directs the

$Cr(CO)_3$ to attack the benzene ring away from the substituted aromatic ring yields the less steric hindered product 2-acetyl-10-nitrophenanthrene (**13**) (see Scheme II).

Bromination

Benz[*a*]anthracene (**1**) in the CCl_4 solution and excess *N*-bromosuccinimide was refluxed for 2 h. After filtration, the residue was chromatographically separated to give brown 7-bromobenz[*a*]anthracene) (**14**) solid (65% yield). The bromination is using NBS as a bromine source in CCl_4 solution, 3-bromobenz[*a*]anthracene (**15**) was obtained from compound **3** *vs* 7-bromobenz[*a*]anthracene (**14**) obtained from uncoordinated benz[*a*]anthracene. The free radical pathway was adapted to explain the difference in the position for brominating in this system. During the bromination of benz[*a*]anthracene, which received an electron, the radical shall be located at the most stable position of benz[*a*]anthracene (i.e., C_8) to accept the bromine radical, yielding compound **14**. On the other hand, the bromination of compound **3**, the presence of the free radical in the $Cr(CO)_3$ coordinated ring can be stabilized by the Cr metal to accept a bromine radical to yield compound **15**. Both radicals are operated in different fashions resulting in different products. However, substituents on the uncoordinated PAH will direct the position for ion coming group according to their nature. Presence of a methyl group (i.e., compound **5**) gave three products (**16**, **17**, **18**) with relatively good yields, while an acetyl group (i.e., compound **10**) led to a single product (**19**) with low yield. The $Cr(CO)_3$ moiety on the PAH will direct a site on the coordinated ring for bromination. The yields of the bromination products are strongly dependent on the nature of the substituent.

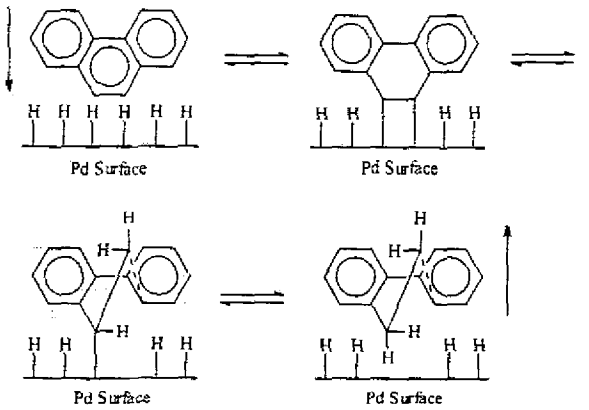


Fig. 1. Mechanism of hydrogenation of polycyclic aromatic hydrocarbons.

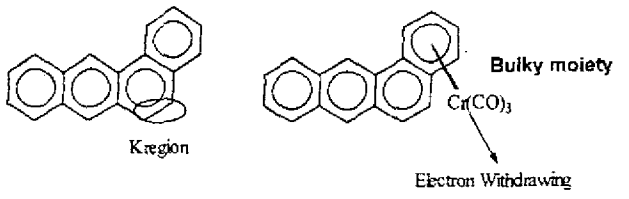


Fig. 2. Deactivation of K region π-electron density.

CONCLUSION

According to this work, we found that the product distributions for reacting the PAH systems (i.e., coordinated PAH and uncoordinated PAH) are strongly dependent on the nature of incoming groups, the substituent, and the presence of $Cr(CO)_3$. Various reaction mechanisms must be operated for the nitration, hydrogenation, and bromination. The results were summarized as follows:

- Hydrogenation of (η^6-arene)tricarbonylchromium does not take place because the electron density of the most electron-rich double bond (the 5,6-position) is decreased to the electron withdrawing moiety-tricarbonylchromium group.
- Nitration of (η^6-arene)tricarbonylchromium exhibits higher selectivity, presumably because of the steric effect of the tricarbonylchromium moiety.
- Bromination of (η^6-arene)tricarbonylchromium results in the bromine attacking on the metal coordinated ring. This may be due to the free radical transfer mechanism.

EXPERIMENTAL SECTION

General Procedures

m.p.s. were taken on a Yanagimoto melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 883 spectrometer. Ultraviolet and visible absorption spectra were recorded on a Shimadzu UV-260 spectrophotometer. Mass spectra were obtained using a JEOL JMS-DX300 spectrometer, with a solid probe inlet, by electron impact with electron energy of 70 eV and a source temperature at 250 °C. ^{1}H NMR spectra were recorded on a Bruker AC-250 spectrometer. The chemical shifts for samples in deuteriochloroform are reported in δ units relative to tetramethylsilane.

Chemicals

Silica gel and all solvents were purchased from Merck Chemical Co. and used without further purification. Chromium hexacarbonyl, *N*-bromosuccinimide, trifluoroacetic acid, anhydrous magnesium sulfate, acetic anhydride, *n*-butyl lithium, 2-methylphenanthrene (**5**), and 2-acetylphenan-

threne (**10**) were purchased from Aldrich Chemical Co..

General Procedure for Preparation of (η^6-Arene)tricarbonylchronium Complexes

(arene = phenanthrene, benz[*a*]anthracene (BA)(**1**)), Benz[*a*]anthracenetricarbonylchromium (**3**), 2-Methylphenanthrenetricarbonylchromium (**9**), 2-Acetylphenanthrenetricarbonylchromium (**12**) were prepared according to procedures previously described.[39]

Hydrogenation of Benz[*a*]anthracene (BA, 1)

Benz[*a*]anthracene (50 mg, 0.22 mmol) in ethyl acetate (30 mL) was hydrogenated in the presence of Pd/C (10%, 40 mg) as a catalyst under H_2 atmosphere (50 psig).[15] After the solution had been magnetically stirred for 24 h at room temperature. Upon filtration through celite, the filtrate was separated chromatographically through silica gel containing 1% of trinitrofluorenone (TNF) with ethyl acetate/hexane as an eluent to give a white solid. 5,6-Dihydrobenz[*a*]anthracene (**2**) giving (22.6 mg, 45%); which was recrystallized from methanol; mp 95-96 °C; UV-visible (CH_2Cl_2) λ_{max} 302 (ε = 16500), 267 (ε = 49970), 258 (ε = 43320), 247 (ε = 28600), 234 (ε = 25600) nm; MS *m/z* (relative intensity) 230 ($[M]^+$, 100), 215 ($[M\text{-}CH_3]^+$, 15), 202 ($[M\text{-}C_2H_4]^+$, 8), 114 ($[M\text{-}C_9H_8]^+$, 28), 108 ($[M\text{-}C_9H_{14}]^+$, 10); ^{1}H NMR δ 2.82 (t, J = 6.6 Hz, 2H, H_5), 2.9 (m, 2H, H_6), 7.08 (t, 1H, J = 1.2 Hz, H_3), 7.16 (t, 1H, J = 7.7 Hz, H_2), 7.31 (dd, 1H, J = 8.3, 6.9 Hz, H_9), 7.4 (d, 1H, J = 7.8 Hz, H_4), 7.4 (dd, 1H, J = 8.3, 6.9 Hz, H_{10}), 7.55 (d, 1H, J = 7.7 Hz, H_1), 7.65 (s, 1H, H_8), 7.78 (d, 1H, J = 8.3 Hz, H_{11}), 7.98 (s, 1H, H_7), and 8.32 (s, 1H, H_{12}).

Hydrogenation of Benz[*a*]anthracenetricarbonylchromium (3)

The same hydrogenation procedure was employed for the hydrogenation of compound **3**, resulting in no reaction based on NMR analysis.

Typical Procedure for Nitration of Either (η^6-Arene)tricarbonylchromium or Polycyclic Aromatic Hydrocarbon

Sodium nitrate (17 mg, 0.2 mmol) in trifluoroacetic acid (15 mL) was added in portions to a solution of benz[*a*]anthracene (45 mg, 0.2 mmol) in acetic acid (50 mL) on an ice bath. After further addition of acetic anhydride (25 mL), the mixture was stirred at 0 °C for 3h. After quenching with ice-water (200 mL) the precipitate was collected by filtrating and washing with water. The residue was separated chromatographically over silical gel with EA/hexane (1:20) as an eluent to yield 7-nitrobenz[*a*]anthracene (**4**) (24 mg, 43% yield); mp 165-167 °C; IR (KBr) 1516, 1366 (ν_{NO2}) cm^{-1}, MS *m/z* (relative intensity) 273 ($[M]^+$, 100), 243 ($[M\text{-}NO]^+$, 54), 227 ($[M\text{-}NO_2]^+$, 48), 215 ($[M\text{-}CNO_2]^+$, 88); ^{1}H NMR δ 7.50 (dd, 1H, J = 8.3, 6.9 Hz, H_3), 7.59 (dd, 1H, J = 8.3, 6.9 Hz, H_2), 7.59 (dd, 1H, J = 8.3, 6.9 Hz, H_{10}), 7.78 (dd, 1H, J = 8.3, 6.9 Hz, H_9), 7.82 (d, 1H, J = 8.3 Hz, H_4), 7.88 (d, 1H, J = 9.0 Hz, H_5), 7.88 (d, 1H, J = 8.3 Hz, H_{11}), 8.03 (d, 1H, J = 9.0 Hz, H_6), 8.15 (d, 1H, J = 8.2 Hz, H_8), 8.40 (m, 1H, H_7), 8.52 (d, 1H, J = 8.5 Hz, H_1), and 8.97 (s, 1H, H_{12}).

Nitration of Benz[*a*]anthracenetricarbonylchromium (3)

Same procedure for the nitration of benz[*a*]anthracene was carried for the nitration of compound **3**. The residue was separated chromatographically over silica gel with EA/hexane (1:20) as an eluent to give 7-nitrobenz[*a*]anthracene (19 mg, 34% yield). The spectra of this product are identical with those of the authentic sample.

From Nitration of 2-Methylphenanthrene (5)

Same procedure for the nitration of benz[*a*]anthracene was carried for the nitration of compound **5**. 2-Methyl-1-nitrophenanthrene (**6**), 2-methyl-4-nitrophenanthrene (**7**) and 2-methyl-9-nitrophenanthrene (**8**) were obtained upon chromatographic separation over silica gel with EA/hexane (1:20) as an eluent. Those resultants were then purified by recrystallization from CH_2Cl_2/hexane. Compound **6** (14 mg, 31% yield); mp 157-158 °C; IR (KBr) 1590, 1380 (ν_{NO2}) cm^{-1}; MS *m/z* (relative intensity) 238 ($[M]^+$, 100), 192 ($[M\text{-}NO_2]^+$, 48), 177 ($[M\text{-}CH_3NO_2]^+$, 88); ^{1}H NMR δ 2.70 (m, 3H, -CH_3), 7.50 (dd, 1H, J = 8.3, 6.9 Hz, H_7), 7.52 (d, 1H, J = 8.8 Hz, H_3), 7.63 (dd, 1H, J = 8.5, 6.9 Hz, H_6), 7.85 (d, 1H, J = 8.3 Hz, H_8). 7.88 (d, 1H, J = 8.4 Hz, H_9), 8.40 (d, 1H, J = 8.4 Hz, H_{10}), 8.54 (d, 1H, J = 8.5 Hz, H_5), and 8.68 (d, 1H, J = 8.8 Hz, H_4). Compound **7** (21 mg, 44% yield); mp 158-159 °C; IR (KBr) 1590, 1390 (ν_{NO2}) cm^{-1}; MS *m/z* (relative intensity) 238 ($[M]^+$, 100), 192 ($[M\text{-}NO_2]^+$, 48), 177 ($[M\text{-}CH_3NO_2]^+$, 88); ^{1}H NMR δ 2.58 (m, 3H, -CH_3), 7.52 (dd, 1H, J = 8.3, 6.9 Hz, H_7), 7.65 (dd, 1H, J = 8.5, 6.9 Hz, H_6), 7.74 (s, 1H, H_3), 7.79 (d, 1H, J = 8.6 Hz, H_9), 7.81 (m, 1H, J = 8.6 Hz, H_{10}), 7.86 (m, 1H, H_1), 7.96 (d, 1H, J = 8.3 Hz, H_8), and 8.73 (d, 1H, J = 8.5 Hz, H_5). Compound **8** (7 mg, 16% yield); mp 156-157 °C; IR (KBr) 1600, 1390 (ν_{NO2}) cm^{-1}; MS *m/z* (relative intensity) 238 ($[M]^+$, 100), 192 ($[M\text{-}NO_2]^+$, 48), 177 ($[M\text{-}CH_3NO_2]^+$, 88); ^{1}H NMR δ 2.54 (m, 3H, -CH_3), 7.38 (d, 1H, J = 8.8 Hz, H_3), 7.66 (dd, 1H; J = 8.5, 6.9 Hz, H_6), 7.85 (m, 1H, H_1), 7.91 (d, 1H, J = 7.4 Hz, H_8), 8.03 (dd, 1H, J = 7.4, 6.9 Hz, H_7), 8.54 (d, 1H, J = 8.8 Hz, H_4), 8.70 (m, 1H, H_{10}), and 8.73 (d, 1H, J = 8.5 Hz, H_5); Anal. Calcd for $C_{15}H_{11}NO_2$: C, 93.16; H, 6.84. Found: C,

93.22; H, 6.71.

From Nitration of 2-Methylphenanthrenetricarbonylchromium (9)

Same procedure was used for nitration of compound **9**. Compound **8** (36 mg, 74% yield) was obtained upon separation over silica gel with EA/hexane (1:20) as an eluent. The spectra of this product are identical with the authetic sample.

From Nitration of 2-Acetylphenanthrene (10)

Same procedure for nitration of benz[*a*]anthracene was used for the nitration of compound **10**. 2-Acetyl-9-nitrophenanthrene (**11**) (18 mg, 36% yield) was obtained upon separation over silica gel with EA/hexane (1:20) as an eluent and recrystallized from methanol; mp 140-141 °C; IR (KBr) 1576, 1390 (ν_{NO2}) cm^{-1}; MS *m/z* (relative intensity) 265 ($[M]^+$, 100), 235 ($[M-NO]^+$, 54), 219 ($[M-NO_2]^+$, 48), 204 ($[M-CH_3NO_2]^+$, 88), 176 ($[M-CH_3CONO_2]^+$, 88); ^1H NMR δ 2.45 (s, 3H, $-CH_3$), 7.67 (dd, 1H, J = 8.5, 6.9 Hz, H_6), 7.92 (d, 1H, J = 7.4 Hz, H_8), 8.03 (dd, 1H, J = 7.4, 6.9 Hz, H_7), 8.05 (d, 1H, J = 8.8 Hz, H_3), 8.71 (s, 1H, H_1), 8.74 (d, 1H, J = 8.8 Hz, H_4), 8.76 (d, 1H, J = 8.5 Hz, H_5), and 8.86 (s, 1H, H_{10}); Anal. Calcd for $C_{16}H_{11}NO_3$: C, 90.85; H, 9.15. Found: C, 90.56; H, 9.11.

From Nitration of 2-Acetylphenanthrenetricarbonylchromium (12)

Same procedure for nitration of benz[*a*]anthracene was performed for nitrating compound **12**. 10-Nitro-2-acetyl-phenanthrene (**13**) (8 mg, 13% yield) was obtained upon separation over silica gel with EA/hexane (1:20) as an eluent and recrystallized from methanol; mp 141-142 °C; IR (KBr) 1600, 1390 (ν_{NO2}) cm^{-1}; MS *m/z* (relative intensity) 265 ($[M]^+$, 100), 235 ($[M-NO]^+$, 54), 219 ($[M-NO_2]^+$, 48), 204 ($[M-CH_3NO_2]^+$, 88), 176 ($[M-CH_3CONO_2]^+$, 88); ^1H NMR δ 2.45 (s, 3H, CH_3), 7.52 (dd, 1H, J = 8.5, 6.9 Hz, H_6), 7.53 (dd, 1H, J = 8.3, 6.9 Hz, H_7), 7.88 (d, 1H, J = 8.3 Hz, H_8), 8.17 (d, 1H, J = 8.8 Hz, H_3), 8.42 (s, 1H, H_1), 8.60 (d, 1H, J = 8.5 Hz, H_5), 8.76 (s, 1H, H_9), and 8.9 (d, 1H, J = 8.9 Hz, H_4); Anal. Calcd for $C_{16}H_{11}NO_3$: C, 90.85; H, 9.15. Found: C, 90.62; H, 9.09.

Typical Procedure for Bromination of Either (η^6-Arene)tricarbonylchromium or Polycyclic Aromatic Hydrocarbon

A CCl_4 solution contains compound **1** (171 mg, 0.75 mmol) and excess *N*-bromosuccinimide (0.2 mg, NBS) was refluxed for 2 h. After filtration, and evaporization to dry, residue was chromatographically separated with EA/hexane (1:20) as an eluent followed by recrystallizaton to give brown solid (145 mg, 65% yield) of 7-bromobenz[*a*]anthracene) (**14**); MS *m/z* (relative intensity) 308 ($[M]^+_{Br81}$, 99), 306 ($[M]^+_{Br79}$, 100), 226 ($[M-HBr_{Br81}]^+$, 69), 224 ($[M-HBr_{Br79}]^+$, 69), ^1H NMR δ 7.45 (dd, 1H, J = 8.3, 6.9 Hz, H_{10}), 7.51 (dd, 1H, J = 8.3, 6.9 Hz, H_3), 7.56 (dd, 1H, J = 9.2, 6.9 Hz, H_9), 7.65 (dd, 1H, J = 8.5, 6.9 Hz, H_2), 7.73 (d, 1H, J = 9.0 Hz, H_5), 7.80 (d, 1H, J = 8.3 Hz, H_{11}), 7.86 (d, 1H, J = 8.3 Hz, H_4), 8.11 (d, 1H, J = 9.2 Hz, H_8), 8.27 (d, 1H, J = 9.0 Hz, H_6), 8.46 (d, 1H, J = 8.5 Hz, H_1), and 8.65 (s, 1H, H_{12}); Anal. Calcd for $C_{18}H_{11}Br$: C, 94.18; H, 5.82. Found: C, 94.01; H, 5.71.

From Bromination of Benz[*a*]anthracenetricarbonylchromium (3)

Same procedure for bromination of compound **1** was used for the bromination of compound **3**. After work-up and recrystallization to yield brown solid (190 mg, 82%) of 3-bromobenz[*a*]anthracene) (**15**); MS *m/z* (relative intensity) 308 ($[M]^+_{Br81}$, 99), 306 ($[M]^+_{Br79}$, 100), 226 ($[M-HBr_{Br81}]^+$, 69), 224 ($[M-HBr_{Br79}]^+$, 69); ^1H NMR δ 7.45 (dd, 1H, J = 8.3, 6.9, H_9), 7.69 (d, J = 8.3 Hz, H_8), 7.71 (d, 1H, J = 8.9 Hz, H_2), 7.73 (d, 1H, J = 8.6 Hz, H_5), 7.74 (dd, 1H, J = 8.3, 6.9, H_{10}), 7.77 (s, 1H, H_4), 7.77 (d, 1H, J = 8.6 Hz, H_6), 7.95 (d, J = 8.3 Hz, H_{11}), 8.1 (s, 1H, H_7), 8.24 (d, 1H, J = 8.9 Hz, H_1), and 8.66 (s, 1H, H_{12}).

From Bromination of 2-Methylphenanthrene (5)

Same procedure for bromination of compound **1** was used to brominate compound **5**. After work-up procedure and separation by chromatographic method, the resultants were identified as 1-bromo-2-methylphenanthrene (**16**), 4-bromo-2-methylphenanthrene (**17**) and 9-bromo-2-methylphenanthrene (**18**). Compound **16** (41 mg, 21% yield); mp 157-159 °C; MS *m/z* (relative intensity) 271 ($[M]^+$, 100), 192 ($[M-Br]^+$, 48), 177 ($[M-CH_3Br]^+$, 88); ^1H NMR δ 2.46 (s, 3H, $-CH_3$), 7.34 (d, 1H, J = 8.8 Hz, H_3), 7.50 (dd, 1H, J = 8.3, 6.9 Hz, H_7), 7.65 (dd, 1H, J = 8.5, 6.9 Hz, H_6), 7.72 (d, 1H, J = 8.4 Hz, H_9), 7.87 (d, 1H, J = 8.3 Hz, H_8), 8.47 (d, 1H, J = 8.7 Hz, H_4, H_5), and 8.18 (d, 1H, J = 8.4 Hz, H_{10}). Compound **17** (68 mg, 33% yield); mp 157-158 °C; MS *m/z* (relative intensity) 271 ($[M]^+$, 100), 192 ($[M-Br]^+$, 48), 177 ($[M-CH_3Br]^+$, 88); ^1H NMR δ 2.47 (s, 3H, $-CH_3$), 7.49 (s, 1H, H_3), 7.55 (dd, 1H, J = 8.5, 6.9 Hz, H_6), 7.56 (dd, 1H, J = 8.3, 6.9 Hz, H_7), 7.72 (d, 1H, J = 8.6 Hz, H_9), 7.73 (d, 1H, J = 8.6 Hz, H_8), 7.76 (d, 1H, J = 8.6 Hz, H_{10}), 7.89 (d, 1H, J = 8.3 Hz, H_1), 8.41 (d, 1H, J = 8.5, H_5), and 8.42 (d, 1H, J = 8.5 Hz, H_4). Compound **18** (23 mg, 11% yield); mp 158-159 °C; MS *m/z* (relative intensity) 271 ($[M]^+$, 100), 192 ($[M-Br]^+$, 48), 177 ($[M-CH_3Br]^+$, 88); ^1H NMR δ 2.55 (s, 3H,

-CH_3), 7.40 (d, 1H, J = 8.8 Hz, H_3), 7.53 (s, 1H, H_1), 7.62 (dd, 1H, J = 8.5, 6.9 Hz, H_6), 7.67 (dd, 1H, J = 8.4, 6.9 Hz, H_7), 8.15 (s, 1H, H_{10}), 8.23 (d, 1H, J = 8.4 Hz, H_8), 8.48 (d, 1H, J = 8.8 Hz, H_4), and 8.52 (d, 1H, J = 8.5 Hz, H_5); Anal. Calcd for $C_{15}H_{11}$: C, 93.16; H, 6.84. Found: C, 93.01; H, 6.68.

Bromination of 2-Methylphenanthrenetricarbonylchromium (9)

Same procedure for bromination of compound **1** was adapted for the bromination of compound **9**. After work-up, the white solid was identified as 4-bromo-2-methylphenanthrene (**17**) (57 mg, 80% yield) by comparison of the spectra with those of the authetic sample.

Bromination of 2-Acetylphenanthrene (10)

Same procedure for bromination of compound **1** was adapted for the bromination of compound **10**. After work-up procedure, the white solid was identified as 2-acetyl-9-bromophenanthrene (**19**) (63 mg, 29% yield); mp 145-147 °C; MS *m/z* (relative intensity) 299 ($[M]^+_{Br81}$, 99), 297 ($[M]^+_{Br79}$, 100), 220 ([M-Br]$^+$, 69), 205 ([M-Br-CH_3]$^+$, 69); ^{1}H NMR δ 2.45 (s, 3H, -CH_3), 7.62 (dd, 1H, J = 8.5, 6.9 Hz, H_6), 7.67 (dd, 1H, J = 8.4, 6.9 Hz, H_7), 8.07 (d, 1H, J = 8.8 Hz, H_3), 8.18 (s, 1H, H_{10}), 8.23 (d, 1H, J = 8.4 Hz, H_8), 8.52 (s, 1H, H_1), 8.62 (d, 1H, J = 8.5 Hz, H_5), and 8.67 (d, 1H, J = 8.8 Hz, H_4); Anal. Calcd for $C_{16}H_{11}Br$: C, 90.85; H, 9.15. Found: C, 90.77; H, 9.03.

Bromination of 2-Acetylphenanthrenetricarbonylchromium (12)

Same procedure for bromination of compound **1** was adapted for the bromination of compound **12**. After work-up process, the white solid was identified as 2-acetyl-7-bromophenanthrene (**20**) (57 mg, 25% yield); mp 146-147 °C; MS *m/z* (relative intensity) 299 ($[M]^+_{Br81}$, 99), 297 ($[M]^+_{Br79}$, 100), 220 ([M-Br]$^+$, 69), 205 ([M-Br-CH_3]$^+$, 69), ^{1}H NMR δ 2.45 (s, 3H, -CH_3), 7.72 (d, 1H, J = 8.9 Hz, H_6), 7.78 (s, 1H, H_8), 7.81 (d, 1H, J = 8.6 Hz, H_{10}), 7.88 (d, 1H, J = 8.6 Hz, H_9), 8.02 (d, 1H, J = 8.8 Hz, H_3), 8.35 (d, 1H, J = 8.9 Hz, H_5), 8.49 (s, 1H, H_1), and 8.64 (d, 1H, J = 8.8 Hz, H_4); Anal. Calcd for $C_{16}H_{11}Br$: C, 90.85; H, 9.15. Found: C, 90.69; H, 9.01.

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Key Words

Hydrogenation; Nitration; Bromination; Arene; Tricarbonyl chromium; Polycyclic aromatic hydrocarbons.

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