Tetrahedron 66 (2010) 4954–4960

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Electronic control of product distribution in the [5+5]-coupling of *ortho*-alkynylbenzaldehyde derivatives and γ,δ-unsaturated carbene complexes

Alejandro Camacho-Davila, Lalith S.R. Gamage, Zhipeng Wang, James W. Herndon *

Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, NM 88003, USA

ARTICLE INFO

Article history:
Received 29 March 2010
Received in revised form 24 April 2010
Accepted 26 April 2010
Available online 22 May 2010

ABSTRACT

The coupling of highly oxygenated *ortho*-alkynylbenzaldehyde derivatives with γ,δ-carbene complexes was evaluated systematically. In all of the electron-rich systems investigated the exclusive product of the reaction is the dihydrophenanthrene derivative. Only the extremely electron-withdrawing methanesulfonate group can prevent this process from occurring. The use of the base additive collidine resulted in a surprising yield enhancement but no other discernable effect on the course of the reaction. Dihydrophenanthrene formation was attributed to rapid dehydration after the opening of a benzo-oxanorbornene intermediate.

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1. Introduction

Polycyclic aromatic hydrocarbons[1] have tremendous applications in materials science and medicinal chemistry. Polycyclic aromatic rings are frequently employed as organic conductors and semiconductors,[2] serve as the core ring structure for several medicinally important compounds,[3] and are useful as fluorescent probes for biological studies.[4] Many polycyclic aromatics derived from combustion are carcinogenic and prevalent in the environment, and chemical derivatives are necessary for studies of their mechanisms of mutagenesis as well as that of their metabolites.[5] Phenanthrenes are among the simplest polycyclic aromatics. The most notable medicinally important phenanthrenoids are the phenanthroindolizidine and phenanthroquinolizidine alkaloids,[6] the aporphine alkaloids,[7] and abietane and kaurane diterpenoids.[8] Phenanthrenoid ring construction[9] is most commonly achieved using precursors where two out of the three rings are intact followed by a cyclization or annulation event. Common approaches to the construction of the phenanthrenoids include electrocyclizations of naphthylcyclobutenones,[10] naphthyl Fischer carbene complex–alkyne couplings,[11] cyclizations of naphthylvinylketene precursors,[12] *cis* stilbene cyclizations,[13] and ring closing metatheses.[14] A unique approach to phenanthrenoid ring systems where two of the three rings are constructed in a single operation is the highlight of the studies in this manuscript.

The coupling of 2-alkynylbenzoyl derivatives (e.g., **1**, Scheme 1) with γ,δ-unsaturated Fischer carbene complexes (**2**) results in the direct synthesis of phenanthrenoid ring systems (e.g., **5**, **6**) in a process where two of the three rings of the phenanthrene system are produced in a single reaction. [15] Hydroxyphenanthrenone **5** is formed as a single diastereomer in a complex tandem process involving the formation of an isobenzofuran (**3**), followed by *exo*-selective[16] intramolecular Diels–Alder reaction (yielding benzo-oxanorbornene **4**), followed by opening of the benzo-oxanorbornene ring system and hydrolysis. The Diels–Alder step is generally more successful for chromium-generated isobenzofurans compared to acid-generated isobenzofurans.[17] In most of the cases examined, hydroxyphenanthrenones of general structure **5** were produced. The dihydrophenanthrenone ring systems (**6**) could be produced after treatment of the crude reaction mixtures with strong acid. In a recent total synthesis of antofine, a dihydrophenanthrene derivative (**8**) was formed directly from the coupling of carbene complex **2** and alkynylbenzoyl derivative **7**.[18] This compound was obtained cleanly after a single chromatography without any acid treatment. Since dihydrophenanthrene formation is likely related to the presence of the electron-donating methoxy groups, a more systematic investigation of this reaction pathway was undertaken.

2. Results and discussion

The general synthetic routes to alkyne-carbonyl compounds from commercially available materials are depicted below in Schemes 2–4 and involve Sonogashira coupling of trimethylsilylacetylene with a suitable benzaldehyde derivative featuring a leaving group in the *ortho*-position as the key step. The precursor to alkyne-aldehyde **1a** (iodide **10**) was obtained through *ortho*

* Corresponding author. Tel.: +1 575 646 2487; fax: +1 575 646 2649; e-mail address: jherndon@nmsu.edu (J.W. Herndon).

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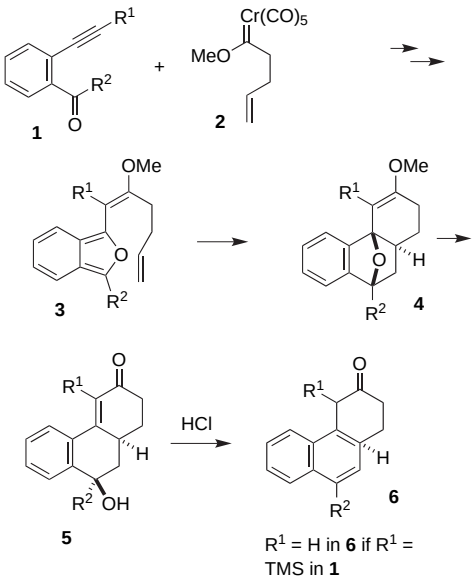
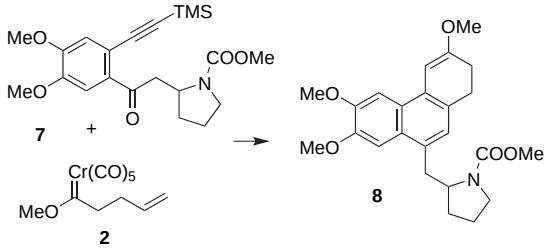
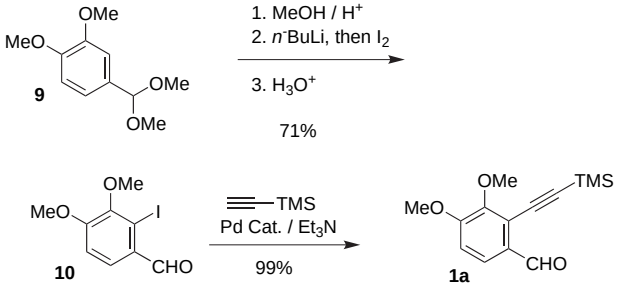
doi:10.1016/j.tet.2010.04.117

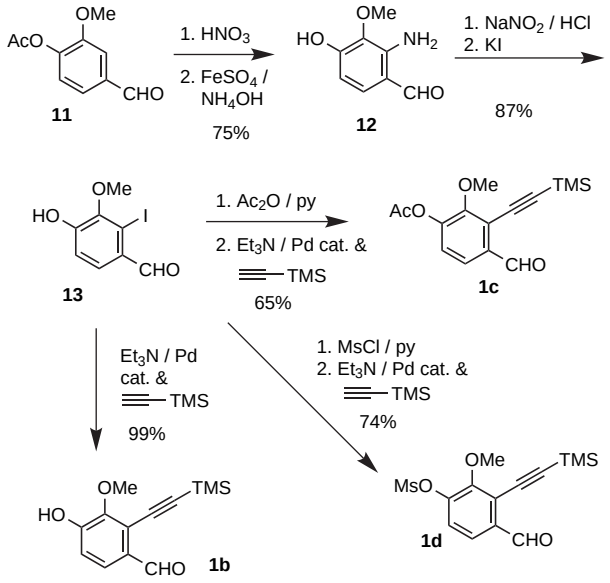




Scheme 1.



Scheme 2.



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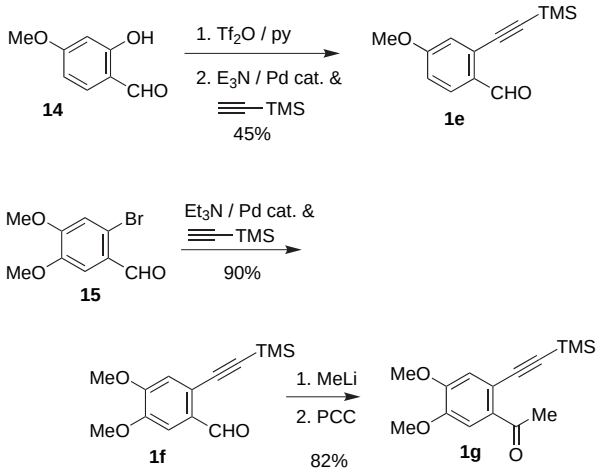
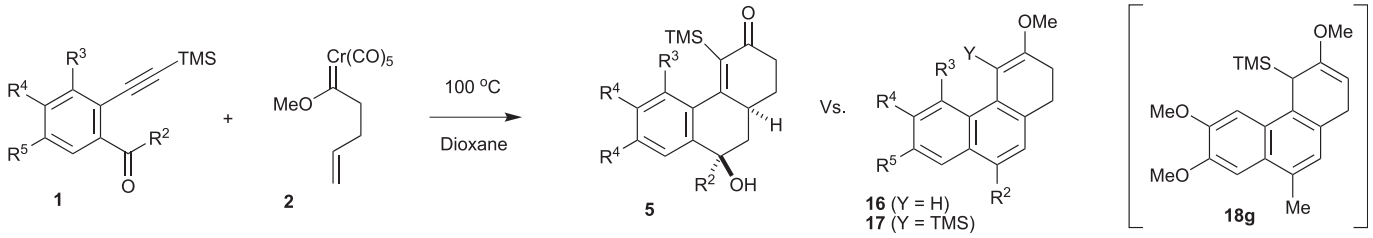


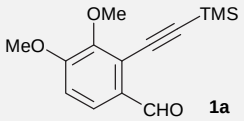
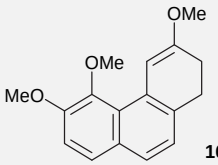
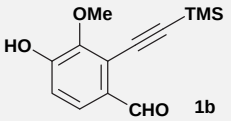
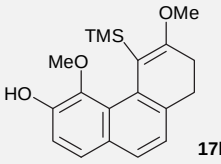
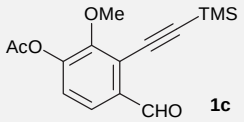
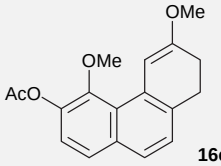
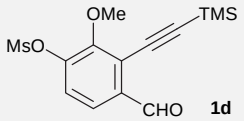
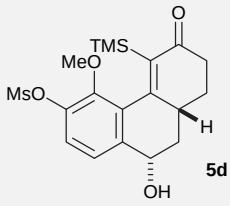
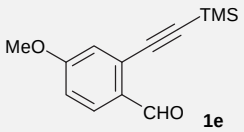
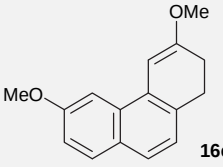
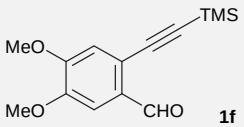
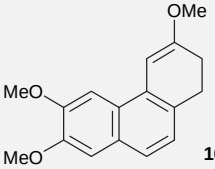
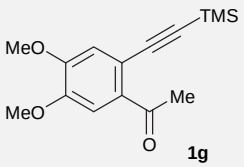
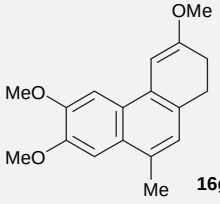
Scheme 4.

metallation/iodination of veratraldehyde dimethyl acetal (**9**) (Scheme 2). Halide precursors to **1b**–**d** were obtained from 2-iodovanillin, which was obtained from vanillin through a known multistep sequence (Scheme 3).[19] Other derivatives were prepared according to the routes depicted in Scheme 4. Monomethoxy derivative **1e** was prepared from commercially available 2-hydroxy-4-methoxybenzaldehyde. Alkyne-carbonyl compounds **1f**–**g** were prepared from commercially available 6-bromoveratraldehyde.

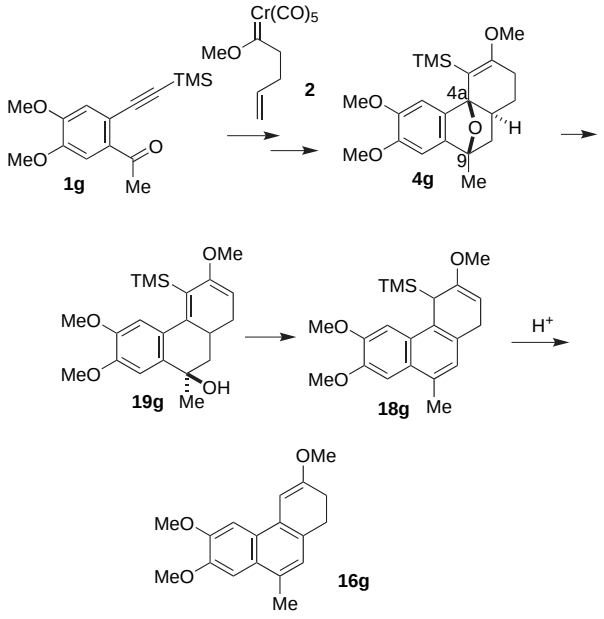
The aromatic ring oxygenated alkynylbenzaldehyde and alkynylacetophenone derivatives were subjected to reaction with carbene complex **2**; the results are depicted in Table 1. In all cases except for entries 2 and 4, the exclusive product after chromatographic purification was dihydrophenanthrene **16**, which results from net dehydration and protiodesilylation. Exclusive formation of the silyl-retained product **17b** (entry 2) was observed in the reaction employing the unprotected phenol **1b**. This observation is somewhat unexpected since steric strain between the methoxy and trimethylsilyl groups is expected to be quite severe in compounds **17a**–**d**. The reaction employing acetate-protected derivative **1c** (entry 3) led primarily to the desilylated compound **16c**, however in several experimental runs varying amounts of the silyl-retained compound **17c** were observed. The hydroxyphenanthrenone derivative **5d** (entry 4) was obtained from the reaction employing the methanesulfonyloxy derivative **1d**. The yield of this latter process was significantly improved if the reaction was conducted using water as a cosolvent. The observed dihydrophenanthrene formation is likely due to activation of the C_9–O bond by the electron-donating methoxy group in the *para*-position and could likely involve *para*-quinonemethide-like intermediates during the dehydration process (see Scheme 5). Entries 1–4 represent a systematic variation in the electron-donating ability of the C_8-activating substituent. The methoxy (entry 1), hydroxyl (entry 2), and the less electron-donating acetoxy groups (entry 3) all result in the dihydrophenanthrenes. Only the severely electron-withdrawing methanesulfonate group[20] (entry 4) results in the hydroxyl-group retained product, **5d**. In one case (entry 7) the crude reaction mixture was examined and a product consistent with allylsilane/enol ether **18g** was observed, however all attempts to

Table 1
Synthesis of dihydrophenanthrenes (**16**–**18**) through coupling of *ortho*-alkynylbenzoyl derivatives (**1**) with Fischer carbene complex **2**

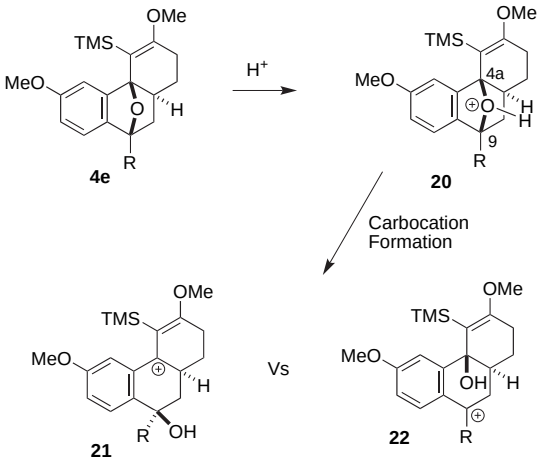


Entry	Alkyne-carbonyl cmpd	Product(s)	Yield (%)
1	 **1a**	 **16a**	58
2	 **1b**	 **17b**	65
3	 **1c**	 **16c**	63[a]
4	 **1d**	 **5d**	52 (72 in 19:1 dioxane/water)
5	 **1e**	 **16e**	57
6	 **1f**	 **16f**	60
7	 **1g**	 **16g**	40 (92 in 9:1 dioxane/collidine)

[a] In some experimental runs variable quantities of silylated compound **17c** were observed.



Scheme 5.



ΔE (R = H)	ΔE (R = Me)
20 to **21** - +1.2	**20** to **21** - +1.9
20 to **22** - +19.8	**20** to **22** - +15.9
21 to **22** - +18.6	**21** to **22** - +14.0

(all values in kcal/mol)

Scheme 6.

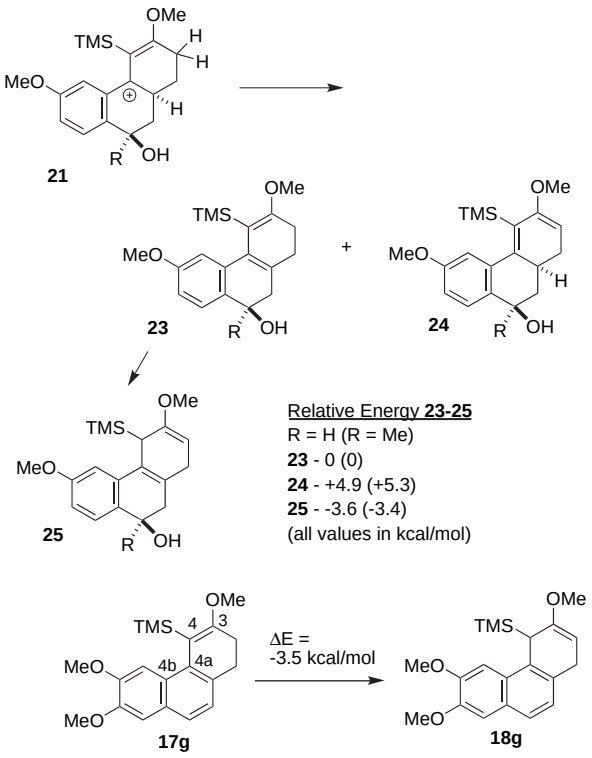
chromatographically purify this compound resulted in its conversion to the desilylated dihydrophenanthrene **16g**.

Interesting proton NMR properties were noted for some of the products in Table 1. For the enol ether protons of **16**, a simple Pascual–Meier–Simon calculation[21] suggests that this proton should have a chemical shift of about δ 5.6 for all of the dihydrophenanthrene examples in the table. This proton occurs at δ 7.24 and 7.11 in adducts **16a** and **16c**, respectively, however occurs at δ 6.1–6.2 in all of the other derivatives of **16** in the table. The chemical shift of compounds **16a** and **16f** was calculated (DFT-B3LYP, 6-31G*) and it was found that the chemical shift of **16a** is predicted to be greater by δ 0.61, perhaps due to the proximity of this hydrogen to oxygen of the bay region methoxy group (2.1 Å in the energy-minimized structure). In all of the desilylated dihydrophenanthrenes (**16**), the $-CH_2CH_2-$ group appears as two triplets, each integrating for two hydrogens. However this same group in compound **17b** appears as four distinct ddd patterns. This is likely due to the nonconjugated arrangement of the enol ether double bond due to steric interaction between the methoxy and trimethylsilyl groups, which results in a chiral compound.

A likely scenario for the conversion of benzo-oxanorbornene intermediate **4** to dihydrophenanthrene derivative **16** is depicted in Scheme 5. Although no acid was deliberately added to the reaction mixture, acid is a necessary component in all of the proposed mechanisms for the conversion of benzo-oxanorbornene intermediates to the corresponding naphthalenes (see Scheme 6). In the absence of acid, coordination of the benzo-oxanorbornene oxygen to a chromium species[22] could serve as a Lewis acid to initiate the ring-opening dehydration sequence. The presence of electron-donating groups *para* to the benzylic alcohol group is expected to facilitate the dehydration step through highly stabilized carbocation intermediates. In order to prevent the dehydration process and prevent formation of carbocation and oxonium ion intermediates, the reaction in entry 7 was examined in the presence of the weakly basic additive collidine. Surprisingly, the reaction in the presence of collidine simply resulted in an enhanced yield of the dihydrophenanthrene derivative **16g** and no alteration of the reaction pathway. The role of collidine is not totally clear, however it is likely related to its ability to serve as a ligand for chromium.[23]

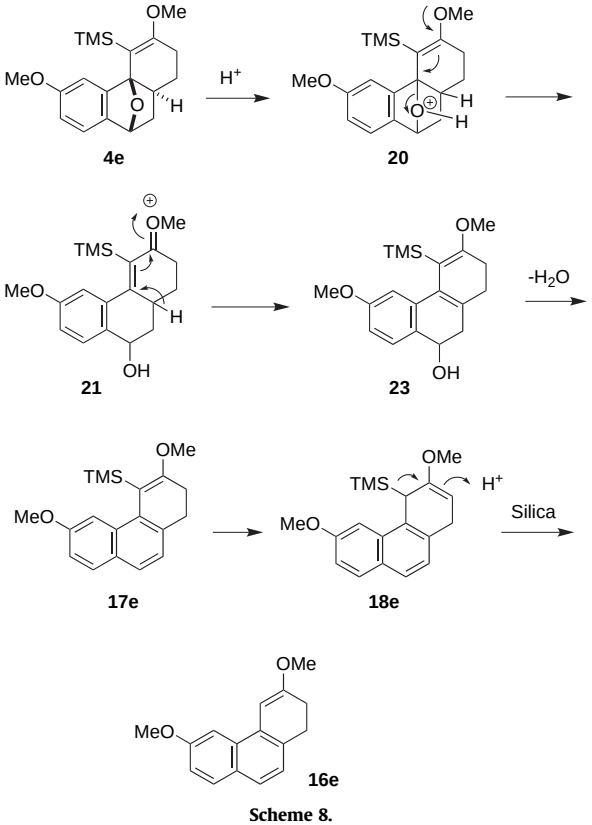
In order to gain further insight into the reaction pathway, the conversion of the benzo-oxanorbornene intermediate to the final product was studied computationally (DFT-B3LYP, 6-31G*). The simplest adduct **4e** was selected for this study to minimize times required for optimization. Protonation of the benzo-oxanorbornene intermediate **4e** to afford intermediate oxonium ion **20** (Scheme 6) followed by ring opening can afford either of the two carbocations **21** or **22**. Minimization of initially formed oxonium ion **20** results in a product where there is significant bond lengthening of the C_{4a}–O bond (2.91 Å) versus the C_9–O bond (1.43 Å). In the neutral benzo-oxanorbornene these bonds are of nearly equal length (C_{4a}–O=1.46 Å; C_9–O=1.44 Å). The minimized structure of **20** has structural features similar to carbocation **21**, and energy minimization results in a product of only slightly higher energy relative to **20**. Carbocation **21** is heavily stabilized through resonance interaction with the enol ether methoxy group. Opening of the oxonium in the other direction to afford *para*-quinonemethide-like species **22** is considerably less favorable. The energetics of benzo-oxanorbornene ring opening are very similar for the cases where R=H or R=Me, however greater stabilization of a tertiary carbocation reduces the energy difference between **21** and **22**.

After the ring-opening process, deprotonation can afford either of conjugated dienes **23** or **24** (Scheme 7). The thermodynamically more favorable compound is isomer **23**. Although **23** is more favored product of simple deprotonation, the isomerization/deconjugation product **25** is even more stable, presumably due to steric interaction of the TMS and aromatic groups in **23**. This difference is even also present in the dehydration products **17g** and **18g**. In the conjugated isomer **17g**, there is minimal overlap of the alkene group and the naphthalene ring system; the C_3–C_4–C_{4a}–C_{4b} dihedral angle is 146° in the energy minimum conformation. Compound **17g** was not observed, however in one experimental run the isomerization product **18g** was observed prior to chromatography. Conversion of enol ether **17g** to the alkene isomer **18g** is unlikely to be a thermal process, however the presence of chromium could serve as a double bond isomerization catalyst.[24] Based on the experimental observation and calculations, the most reasonable pathway for conversion of oxanorbornenes to aromatic systems is depicted in Scheme 8, and



Scheme 7.

involves opening to the carbocation/oxonium ion species **21**, followed by deprotonation to afford the hydrated naphthalene derivative **23**. Water loss and energetically favorable deconjugation affords the allylsilane/enol ether. The final product then results from protiodesilylation to afford the observed dihydrophenanthrene products.



Scheme 8.

3. Conclusions

The coupling of γ,δ-unsaturated carbene complexes with 2-alkynylbenzaldehyde/acetophenone derivatives featuring electron-rich oxygenated aromatic ring systems leads to dihydrophenanthrenes in a net [5+5]-cycloaddition involving sequential carbene complex–alkyne coupling, isobenzofuran formation, and intramolecular Diels–Alder reaction. The net coupling process is an intermolecular one, which is inherently superior to methods based on intramolecular systems. The initially formed benzo-oxanorbornenes undergo net dehydration and desilylation processes, which are enhanced by the presence of electron-donating groups. Electron-withdrawing methanesulfonyloxy groups suppress the dehydration pathway and result in hydroxyphenanthrenone derivative.

4. Experimental[25]

4.1. General procedure for carbene complex–alkyne coupling

To a refluxing 0.1 M solution of the alkyne-aldehyde/ketone (1 equiv) in dioxane (10 mL/mmol) was added over a 1 h period a solution of carbene complex **2** (1.2 equiv) in dioxane (10 mL/mmol). After the addition, the reflux was continued for 24 h and the mixture was allowed to reach room temperature. The dioxane was removed on a rotary evaporator and the residue was suspended in hexane/ethyl acetate and filtered through Celite. The filtrate was concentrated under reduced pressure and the residue purified by flash chromatography on silica gel.

4.2. Coupling of carbene complex 2 with aldehyde 1a (Table 1, entry 1)

The general procedure was followed using carbene complex **2** (348 mg, 1.20 mmol) and aldehyde **1a** (265 mg, 1.00 mmol). Final purification was achieved by flash chromatography on silica gel using 4:1 hexane/ethyl acetate as eluent. Dihydrophenanthrene **16a** was isolated (158 mg, 58% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.53 (d, 1H, J=8.7 Hz), 7.44 (d, 1H, J=8.1 Hz), 7.24 (br s, 1H), 7.21 (d, 1H, J=8.7 Hz), 7.12 (d, 1H, J=8.1 Hz), 3.98 (s, 3H), 3.82 (s, 3H), 3.81 (s, 3H), 2.99 (t, 2H, J=6.7 Hz), 2.44 (t, 2H, J=6.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 149.8, 144.9, 130.2, 129.5, 125.5, 125.1, 124.8, 124.6, 124.5, 113.6, 96.3, 61.0, 56.8, 54.6, 30.1, 26.5; MS (EI): 270 (M^+, 100), 255 (52), 240 (12), 224 (16), 212 (33); HRMS (EI): calcd for $C_{17}H_{18}O_3$ 270.1256, found 270.1265.

4.3. Coupling of carbene complex 2 with aldehyde 1b (Table 1, entry 2)

The general procedure was followed using carbene complex **2** (346 mg, 1.20 mmol) and aldehyde **1b** (248 mg, 1.00 mmol). Final purification was achieved by flash chromatography on silica gel using 4:1 hexane/ethyl acetate as eluent. Dihydrophenanthrene **17b** was isolated (214 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, 2H, J=8.0 Hz), 7.18 (d, 1H, J=8.0 Hz), 7.14 (d, 2H, J=8.0 Hz), 5.98 (s, 1H), 3.73 (s, 3H), 3.57 (s, 3H), 2.85 (ddd, 1H, J=15.0, 14.7, 6.3 Hz), 2.74 (ddd, 1H, J=15.0, 6.3, 2.0 Hz), 2.53 (ddd, 1H, J=15.0, 5.3, 2.0 Hz), 2.21 (ddd, 1H, J=15.0, 14.7, 5.3 Hz), 0.02 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 165.8, 145.4, 140.5, 134.4, 131.6, 129.8, 125.2, 125.1, 123.4, 116.9, 115.5, 60.6, 55.8, 30.6, 22.9, 1.2; HRMS (ESI): calcd for $C_{18}H_{25}O_3Si$ (M+H) 329.1573, found 329.1573.

4.4. Coupling of carbene complex 2 with aldehyde 1c (Table 1, entry 3)

The general procedure was followed using carbene complex **2** (348 mg, 1.20 mmol) and aldehyde **1c** (277 mg, 1.00 mmol). Final purification was achieved by flash chromatography on silica gel using 4:1 then 2:1 hexane/ethyl acetate as eluent. Compound **16c** was isolated (188 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, 1H, J=8.8 Hz), 7.49 (d, 1H, J=8.2 Hz), 7.23 (d, 1H, J=8.2 Hz), 7.11 (d, 1H, J=8.8 Hz), 7.09 (br s, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.00 (t, 2H, J=7.6 Hz), 2.44 (t, 2H, J=7.6 Hz), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 160.3, 148.2, 141.2, 133.7, 130.8, 130.6, 126.5, 125.4, 124.3, 124.2, 120.6, 96.0, 61.6, 54.7, 30.0, 26.5, 20.8; IR (neat): 1764 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{19}O_4$ (M+H) 299.1278, found 299.1288.

4.5. Coupling of carbene complex 2 with aldehyde 1d (Table 1, entry 4)

The general procedure was followed using carbene complex **2** (290 mg, 1.00 mmol) and aldehyde **1d** (326 mg, 1.00 mmol) in 19:1 dioxane/water (10 mL). Final purification was achieved by flash chromatography on silica gel using 4:1 followed by 1:1 hexane/ethyl acetate as eluent. Compound **5d** was isolated (300 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, 1H, J=8.1 Hz), 7.08 (d, 1H, J=8.1 Hz), 4.93 (t, 1H, J=6.6 Hz), 3.63 (s, 3H), 3.30 (s, 3H), 2.60–2.50 (m, 2H), 2.34 (ddd, 1H, 17.0, 13.8, 4.3 Hz), 2.26 (ddd, 1H, J=12.9, 8.8, 4.3 Hz), 2.17 (ddd, 1H, J=13.8, 9.6, 3.8 Hz), 2.02–1.90 (m, 2H), 1.85 (br s, 1H), 0.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.2, 160.3, 149.7, 142.4, 142.0, 141.4, 132.4, 125.0, 122.6, 69.0, 60.7, 39.2, 37.8, 37.6, 36.4, 31.4, 0.0; IR (neat): 3409, 1645 cm^{-1}; Mass Spec (FAB): 433 (M+Na, 16), 411 (M+H, 16), 395 (100); HRMS: calcd for $C_{19}H_{27}O_6SSi$ (M+H) 411.1298, found 411.1282.

4.6. Coupling of carbene complex 2 with aldehyde 1e (Table 1, entry 5)

The general procedure was followed using carbene complex **2** (221 mg, 0.76 mmol) and aldehyde **1e** (161 mg, 0.69 mmol). Final purification was achieved by flash chromatography on silica gel using 4:1 hexane/ethyl acetate as eluent. Compound **16e** was isolated (95 mg, 57%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.72 (d, 1H, J=8.8 Hz), 7.50 (d, 1H, J=8.2 Hz), 7.32 (d, 1H, J=2.2 Hz), 7.16 (d, 1H, J=8.2 Hz), 7.13 (dd, 1H, J=8.8, 2.4 Hz), 6.17 (s, 1H), 3.98 (s, 3H), 3.88 (s, 3H), 3.05 (t, 2H, J=8.2 Hz), 2.52 (t, 2H, J=8.2 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 161.0, 157.46, 130.1, 130.0, 129.4, 129.2, 128.5, 124.1, 116.7, 101.8, 91.6, 55.3, 54.8, 29.6, 29.5, 27.5; IR (neat): 1657 (s), 1621 (s) cm^{-1}; Mass Spec (EI): 240 (M, 100), 225 (45); HRMS (EI): calcd for $C_{16}H_{16}O_2$ 240.1150, found 240.1148.

4.7. Coupling of carbene complex 2 with aldehyde 1f

The general procedure was followed using carbene complex **2** (450 mg, 1.55 mmol) and aldehyde **1f** (375 mg, 1.29 mmol). Final purification was achieved by flash chromatography on silica gel using 4:1 hexane/ethyl acetate as eluent. Compound **16f** was isolated (242 mg, 60%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.38 (d, 1H, J=8.1 Hz), 7.24 (s, 1H), 7.12 (s, 1H, J=8.1 Hz), 7.07 (s, 1H), 6.10 (s, 1H), 4.03 (s, 3H), 3.98 (s, 3H), 3.81 (s, 3H), 3.00 (t, 2H, J=8.8 Hz), 2.47 (t, 2H, J=8.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 161.2, 149.3, 148.8, 129.2, 128.8, 127.4, 124.7, 122.9, 107.2, 101.9, 91.8, 55.9, 55.8, 54.9, 29.6, 27.7; MS (EI): 270 (M, 100), 255 (38), 227 (27); HRMS (EI): calcd for $C_{17}H_{18}O_3$ 270.1256, found 270.1251.

4.8. Coupling of carbene complex 2 with ketone 1g

The general procedure was followed using carbene complex **2** (300 mg, 1.03 mmol) and ketone **1g** (280 mg, 1.00 mmol). Final purification was achieved by flash chromatography on silica gel using 4:1 followed by 3:2 hexane/ethyl acetate as eluent. Compound **16g** was isolated (115 mg, 40%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.30 (s, 1H), 7.18 (s, 1H), 7.03 (s, 1H), 6.11 (s, 1H), 4.06 (s, 3H), 4.03 (s, 3H), 3.86 (s, 3H), 2.98 (t, 2H, J=8.8 Hz), 2.60 (s, 3H), 2.48 (t, 2H, J=8.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 160.5, 148.9, 148.5, 128.8, 127.6, 127.4, 127.2, 126.0, 124.8, 103.7, 102.5, 91.8, 55.9, 55.7, 54.8, 29.5, 27.7, 19.6; MS (EI): 284 (M, 100), 269 (54), 241 (30); HRMS (EI): calcd for $C_{18}H_{20}O_3$ 284.1412, found 284.1407. If one omits the chromatography step a different product consistent with **18g** was obtained in greater than 90% purity: ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.21 (s, 1H), 7.19 (s, 1H), 7.03 (s, 3H), 4.79 (br d, 1H, J=4.0 Hz), 4.03 (s, 6H), 3.65 (s, 3H), 3.65–3.30 (m, 3H), 2.89 (s, 3H), 0.03 (s, 9H).

4.9. Coupling of carbene complex 2 with ketone 1g in 10:1 dioxane/collidine

A modification of the general procedure was followed using carbene complex **2** (430 mg, 1.50 mmol) and ketone **1g** (280 mg, 1.00 mmol) in collidine (1 mL) and dioxane (10 mL) at 80 °C. After a 24 h period at 80 °C, the mixture was cooled to room temperature and filtered through a thin layer of Celite and the solvent was removed on a rotary evaporator. The residue was dissolved in dichloromethane and washed with saturated aqueous ammonium chloride solution and then dried over sodium sulfate. The solution was concentrated under reduced pressure and then purified by flash chromatography on silica gel using 14:1 hexane/ethyl acetate as an eluent to afford compound **16g** (260 mg, 92%).

Acknowledgements

This work was supported by the SCORE program of NIH (SC1GM083693).

Supplementary data

Detailed experimental procedures for syntheses of alkyne-carbonyl compounds from commercially available materials, copies of ^{1}H NMR and ^{13}C NMR data for products in Table 1, and computational details and SCF energies for structures depicted in Schemes 6 and 7. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.04.117. These data include MOL files and InchIkeys of the most important compounds described in this article.

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