Metal-Catalyzed Cyclopropene Rearrangements for Benzannulation: Evaluation of an Anthraquinone Synthesis Pathway and Reevaluation of the Parallel Approach via Carbene–Chromium Complexes

M. F. Semmelhack,*,† Suzzy Ho,† D. Cohen,† M. Steigerwald,† M. C. Lee,† G. Lee,† Adam M. Gilbert,‡ William D. Wulff,*,‡ and Richard G. Ball§

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08544, Department of Chemistry, Searle Chemistry Laboratory, The University of Chicago, Chicago, Illinois 60637, and Merck Research Laboratories, Division of Merck and Company, Inc., Box 2000, Rahway, New Jersey 07065-0900

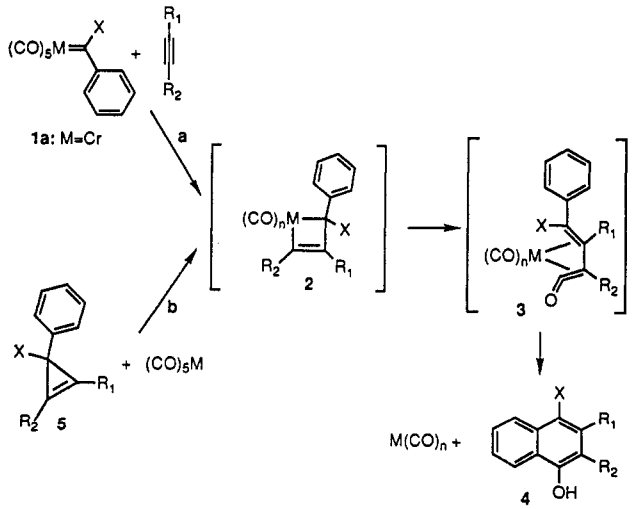
Received March 25, 1994®

Abstract: The reaction of 3-arylcyclopropenes with $Cr(CO)_6$ and $Mo(CO)_6$ produces naphthols, in an example of metal-promoted benzannulation. Substituents at C-3 (in addition to aryl) have a strong effect on the success of the process: 3-H derivatives are generally effective, but the yields decrease for 3-alkyl derivatives as the size of the alkyl group increases. The 3,3-diphenyl and 3-cyano derivatives are unreactive. The mechanism is postulated to involve metal-complexed vinyl carbene units, parallel with the benzannulation reaction involving arylcarbene complexes with alkynes. The regioselectivity has been probed with various unsymmetrically 1,2-disubstituted 3-arylcyclopropenes. The results suggest a simple correlation with steric size, consistent with initial cleavage of the cyclopropene σ bond bearing the smaller substituent. The result of this regioselectivity is a product structure showing a substituent arrangement opposite to that from the carbene–chromium approach; the smaller substituent of the cyclopropyl double bond ends up adjacent to the phenol OH in the product. Catalytic activity at low efficiency was observed, using a $Mo(CO)_6$ catalyst. However, the use of $Mo(CO)_6$ also promotes formation of indenes as significant byproducts at the expense of naphthalenes. Attempts to use the arylcyclopropene rearrangement to convert a 3-(1,4-dimethoxy-2-naphthyl)-cyclopropene to an anthraquinone skeleton produced instead a phenanthrene via an unusual substitution for a methoxy substituent. A related example previously reported to produce anthraquinones via the naphthylcarbene-chromium/alkyne reaction was shown to be in error; the correct structure is again a phenanthrone, and the product is exactly parallel with that observed in the cyclopropene rearrangement. A *naphthoquinone* substituted with a cyclopropene at C-2 does provide the first example of metal-promoted benzannulation to give an anthraquinone.

Introduction

In recent years there have been remarkable advances in methods of construction of aromatic rings (benzannulation) based generally on cyclization of vinylketene intermediates and related cycloaddition strategies.[1-7] The interaction of a carbene–chromium complex (**1a**) with an alkyne and CO, first described by Dötz and Kreiter,[1a] has led to numerous extensions and applications in the synthesis of quinone derivatives.[1,2,3] The process is believed to begin by cycloaddition of the alkyne with the carbene ligand (in **1**) to generate a vinylcarbene[8] or metallacyclobutene (**2**) complex, followed by CO insertion to give a key vinylketene (**3**) and final cyclization to a hydroquinone **4** (usually as the η^6-chromium complex (Scheme 1, path a).[2] There are significant limitations on the carbene + alkyne approach: (a) stoichiometric quantities of chromium are required and there is no realistic pathway for *in situ* recycling of the Cr(0) byproduct; (b) general success has been obtained only with alkoxy-substituted carbene ligands, leading specifically to 1,4-hydroquinones. A special case is the analogous amino–carbene chromium complexes which appear to follow a related pathway, giving indenes as the major products.[9,10] Indenes often appear as minor products in the benzannulation process.

Scheme 1. Mechanistic Relationship of Carbene/Alkyne and Cyclopropene Rearrangement Benzannulations



We have been interested in alternative conditions for metal-promoted benzannulation which hold the possibility of catalysis and/or the use of less noxious metals. A simple alternative for the formation of the metallacyclobutene complex (**2**; or the corresponding η^1,η^3-vinylcarbene complex) is direct insertion of low-valent metals into a 3-arylcyclopropene (e.g., **5**) C—C σ bond (Scheme 1). Then the same CO insertion would give a

† Princeton University.
‡ The University of Chicago.
§ Merck Research Laboratories.
® Abstract published in *Advance ACS Abstracts,* July 1, 1994.

(1) (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644. (b) Dötz, K. H.; Popall, M. *Tetrahedron* **1985**, *41*, 5797.
(2) (a) Wulff, W. D. In *Comprehensive Organic Synthesis;* Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1990; Vol. 5, p 1065. (b) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press, Inc.: Greenwich, CT, 1989; Vol. 1.
(3) Semmelhack, M. F.; Bozell, J. J.; Keller, L.; Sato, T.; Spiess, E. J.; Wulff, W. D.; Zask, A. *Tetrahedron* **1985**, *41*, 5803.
(4) Danheiser, R. L.; Brisbois, R. G.; Kowalczyk, J. J.; Miller, R. F. *J. Am. Chem. Soc.* **1990**, *112*, 3093.

0002-7863/94/1516-7108$04.50/0

vinylketene complex (**3**) and allow rearrangement to a naphthol (**4**). In principle, the low-valent metal is the same as the metal byproduct from the quinone synthesis, assuming CO is used in excess.

The interaction of cyclopropenes with transition metals has been an active area since the original attempts to produce an η^3-cyclopropenyl–metal complex.[11] This led to observation of direct insertion of $Fe(CO)_5$ into a ring C—C bond of tetramethylcyclopropene under surprisingly mild conditions for cleavage of a carbon–carbon bond; the first intermediate detected is a vinylketene complex.[12] Numerous transition metals have been reported to undergo parallel reactions, with the conspicuous exception of the chromium triad: Cr, Mo, and W. None of the known vinylketene ligands formed from cyclopropenes have been reported to rearrange to arene rings.[13] Acylcyclopropenes are also reactive toward insertion of a transition metal and lead to hydroquinone derivatives[14] or phenols.[15]

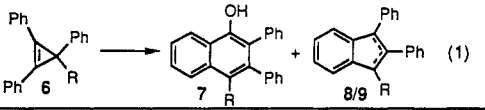
In this paper, we report studies of the feasibility of benzannulation using 3-arylcyclopropenes with Cr(0) and Mo(0) and consider in detail the particular case of the annulation of naphthalene derivatives into anthraquinones of significance as antitumor agents. The unexpected formation of phenanthrene products instead of anthraquinones has prompted close examination of the parallel carbene + alkyne approach to the same intermediates, and a revision of earlier observations[1b,16,17] is required.

Results and Discussion

Scope and Limitations of the Cyclopropene Rearrangement. We chose the readily accessible series of 3-substituted-1,2,3-triphenylcyclopropenes (**6**) in order to probe the reactivity toward $Cr(CO)_6$ and $Mo(CO)_6$. Compounds **6** were prepared by addition of the appropriate nucleophile[18,19] ($LiAlH_4$, PhMgBr, MeMgI, EtMgBr, iPrMgBr, NaCN) to triphenylcyclopropenium tetrafluoroborate. As presented in eq 1 and Table 1, disappearance of the starting cyclopropene in the presence of stoichiometric amounts of $Cr(CO)_6$ is relatively slow (100–145 °C) compared to the analogous alkyne + carbene–Cr reaction (typically 60–80 °C), but the product type is the same. Entry 1 shows conversion of **6**, R = OMe, into 3,4-diphenyl-1,4-naphthohydroquinone monomethyl ether (**7**, R = OMe) in 62% yield, in direct analogy to the reaction of (phenyl(methoxy)methylidene)$Cr(CO)_5$ with diphenylacetylene to give the same product.[1a,20] Reasonable rates were obtained with stoichiometric amounts of $Cr(CO)_6$ only at elevated temperatures, and no intermediates were detected.

Replacement of the 3-methoxy group has a strong effect on the rate. The reaction is much slower with tetraphenylcyclopropene (entry 10), showing only 5% conversion to **7**, R = Ph, after 20 h in di-*n*-butyl ether at reflux (145 °C). With the electron-withdrawing cyano substituent in the 3-position (**6**, R = CN), no product (**7**, R = CN) was detected after 48 h at reflux at 145 °C (entry 12). A C-3 methyl substituent (**6**, R = Me) also lowers the rate, showing 76% conversion after 20 h at 145 °C and a yield of only 27%; no other significant product was identified (entry 5). With a C-3 hydrogen substituent (**6**, R = H, entry 2), the reaction proceeds at a rate comparable to the OMe case, but the yield is again only 45%. There is no direct comparison with the alkyne + carbene–metal reaction, since the carbene–metal process requires an alkoxy group at the carbene carbon.

Table 1. Rearrangement of 1,2,3-Triphenylcyclopropenes



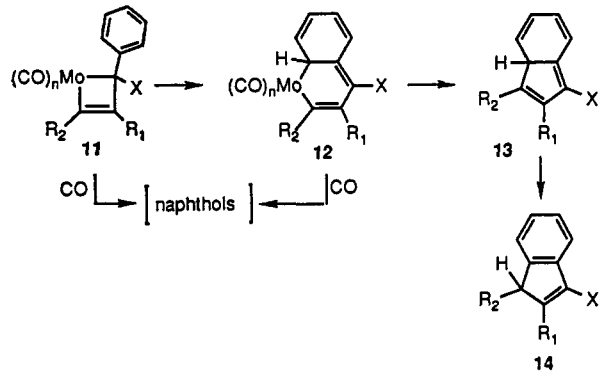
entry	R	metal	conditions	yield **7** (%)	yield **8/9** (%)	SM rec (%)
1	OMe	Cr	nBu_2O, reflux, 3 h	62	0	0
2	H	Cr	nBu_2O, reflux, 3 h	45	0	0
3	H	Mo	dioxane, reflux, 1 h	78	11	0
4	H	W	dioxane, reflux 22 h	19	34	32
5	Me	Cr	nBu_2O, reflux, 20 h	27	0	24
6	Me	Mo	dioxane, reflux, 1 h	30	70	0
7	Me	Mo	dioxane, reflux, 2 h[a]	27	42	0
8	Et	Mo	dioxane, reflux, 2 h	18	73	0[b]
9	iPr	Mo	dioxane, reflux, 7.5 h	8	71	0[c]
10	Ph	Cr	nBu_2O, reflux, 20 h	5	0	95
11	Ph	Mo	nBu_2O, reflux, 2 h	21	75	0
12	CN	Cr	nBu_2O, reflux, 4–48 h	0	0	84

[a] Under 1.1 atm of CO. All other examples are under argon. [b] A cyclobutenone was isolated in 7% yield (see text). [c] A cyclobutenone was isolated in 17% yield (see text).

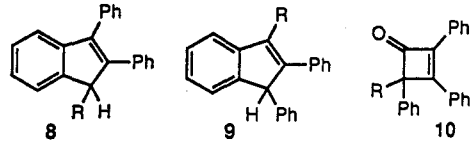
The reaction rates are higher with $Mo(CO)_6$, the faster cases proceeding to completion within 1 h in dioxane at reflux. The yield with the C-3 H substituent (**6**, R = H) is good (entry 3; 78% yield of 2,3-diphenyl-1-naphthol; **7**, R = H), but in all other cases, production of indenes becomes significant, (**8/9**, as a mixture of two alkene positional isomers). Since cyclopropenes with 3-phenyl substituents are known[21] to rearrange to indenes thermally or under acid- and metal-catalyzed conditions, it was necessary to show that the rearrangement in the absence of metal is not responsible for the indene observed. Control experiments were carried out to show that, under the reaction conditions for the metal-catalyzed rearrangement (dioxane, 101 °C, 3 h), the uncatalyzed rate of conversion of the cyclopropenes **6**, R = OMe and Me, was slower ($t_{1/2}$ > 24 h at 101 °C). The formation of indenes as major products was also noted in one reaction with $W(CO)_6$ (entry 4), but is clearly not significant in the series with $Cr(CO)_6$. Another minor product is the cyclobutenone structure (**10**), which appeared from **6**, R = Et (7%) and iPr (17%), suggesting that larger alkyl substituents at C-3 favor this product[22] and that the cyclobutenones appear at the expense of the naphthol products **7**. The major indene isomer (**8**) from **6**, R = Me, Et, iPr, and Ph, could be isolated by chromatography, and each was fully characterized. The amount of other isomer was estimated

(5) Krysan, D. K.; Gurski, A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1992**, *114*, 1412.
(6) Perri, S. T.; Moore, H. W. *J. Am. Chem. Soc.* **1990**, *113*, 1897.
(7) Liebeskind, L.; Cho, S. H. *J. Org. Chem.* **1987**, *52*, 2631.
(8) Theoretical studies suggest that the reaction with the alkyne leads directly to the formation of an η^1,η^3-vinyl carbene complexed intermediate: (a) Hofmann, P.; Hämmerle, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 908. (b) Hofmann, P.; Hämmerle, M.; Unfried, G. *New. J. Chem.* **1991**, *15*, 769.
(9) Yamashita, A. *Tetrahedron Lett.* **1986**, *28*, 5915
(10) Deactivated amino carbene complexes do give phenol products: Grotjahn, D. B.; Kroll, F. E. K.; Schaefer, T.; Harms, K.; Dötz, K. H. *Organometallics*, **1992**, *11*, 298.
(11) Coffey, C. E. *J. Am. Chem. Soc.* **1962**, *84*, 118.
(12) King, R. B. *Inorg. Chem.* **1963**, *2*, 642.
(13) Weiss, E.; Klimes, J. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 205.
(14) Liebeskind, L. S.; Cho, S. H. *J. Org. Chem.* **1987**, *52*, 2631.
(15) Benzannulation is observed in one special case from Rh(I)-catalyzed rearrangement of 3-acylcyclopropenes in the presence of a silylacetylene: Padwa, A.; Xu, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 5881.
(16) Bos, M. E.; Wulff, W. D.; Miller, R. A.; Chamberlin, S.; Brandvold, T. A. *J. Am. Chem. Soc.* **1991**, *113*, 9293. While the initial report of the formation of **7**, R = OMe, by the chromium–carbene/alkyne cycloaddition states a yield of 62% and recovered starting material, the yield can be 89–94% at complete conversion.
(17) (a) Doetz, K. H.; Popall, M. *J. Organomet. Chem.* **1985**, *291*, C1; (b) Doetz, K. H.; Popall, M. *Chem. Ber.* **1988**, 665.
(18) Doetz, K. H. *Chem. Abs.* **1985**, *104*, 168270c.
(19) (a) Breslow, R.; Lockhart, J.; Chang, H. W. *J. Am. Chem. Soc.* **1961**, *83*, 2375. (b) Breslow, R.; Dowd, P. *Ibid.* **1963**, *85*, 2729. (c) Breslow, R.; Yuan, C. *Ibid.* **1958**, *80*, 5991.
(20) Zimmerman, H. E.; Assen, S. M. *J. Org. Chem.* **1978**, *43*, 1493.
(21) (a) Breslow, R. In *Molecular Rearrangements*; de Mayo, P., Ed.; Interscience: New York, 1963; Part 1, p 257. (b) McCullough, J. *Can. J. Chem.* **1968**, *46*, 43. (c) Battiste, A.; Halton, B.; Grubbs, R. H. *Chem. Commun.* **1967**, 907. (d) Walker, J. A.; Orchin, M. *Ibid.* **1968**, 1239.
(22) For a discussion of a possible source of this effect in other examples, see: Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, *334*, 9.

Scheme 2. Mechanism of Formation of Indenes

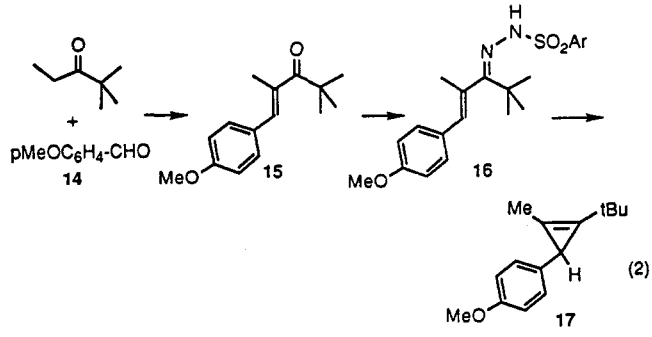


from the signal at the characteristic chemical shift of the tertiary hydrogen in **9** compared to **8**.



Indenes can be significant products in the alkyne + carbene–metal hydroquinone synthesis[2] and are the major products from amino–carbene complexes.[9] Their formation from the expected metallacyclobutene intermediate (**11**) can be understood as a ring expansion to give the metallonaphthalene (**12**), which then can undergo reductive elimination to the isoindene **13**. Rapid H shifts complete the process to give general indene **14** (Scheme 2). The ring expansion can be in competition with a CO insertion step, to give the vinylketene complex and eventually the usual hydroquinone. It is not clear why indenes are important in the Mo-promoted reactions and not at all in the Cr series.[23] On the basis of the mechanism proposed here, it seemed reasonable to expect that higher CO concentration could favor the CO insertion product (leading to naphthohydroquinone). However, CO at 1.1, 2.5, and 4.5 atm had the effect of inhibiting the reaction, presumably by inhibiting CO dissociation from the starting $Mo(CO)_6$, and did not produce a larger fraction of the CO insertion product.

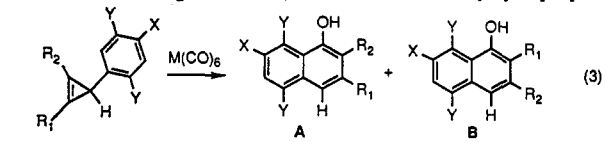
Naphthol formation is the major process using cyclopropene **6**, R = H, with $Mo(CO)_6$ and with a series of variously substituted cyclopropenes (e.g., **17**) all bearing a C-3 hydrogen substituent (Table 2). This set was prepared by the rearrangement of a tosylhydrazone (e.g., **16**) derived from an aryl vinyl ketone (**15**, illustrated in eq 2).[17]



Simple alkyl substituents on the cyclopropene double bond are compatible with the cyclopropene rearrangement. The issue of regioselectivity arises in Table 2. In the limited number of cases

(23) For a study of the effect of the metal on the benzannulation reaction, see: Wulff, W. D.; Bax, B. M.; Brandvold, T. A.; Chan, K. S.; Gilbert, A. M.; Hsung, R. P.; Mitchell, J. Clardy, J., *Organometallics* **1994**, *13*, 102.
(24) Monahan, A.; Lewis, D. *J. Chem. Soc., Perkin Trans. 1*, **1977**, 60.

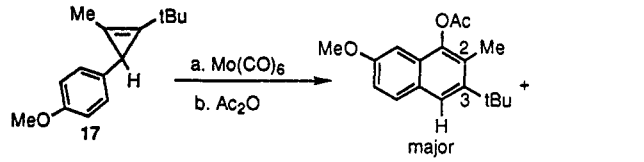
Table 2. Rearrangement of 1,2-Disubstituted 2-Arylcyclopropenes

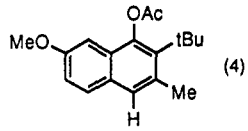


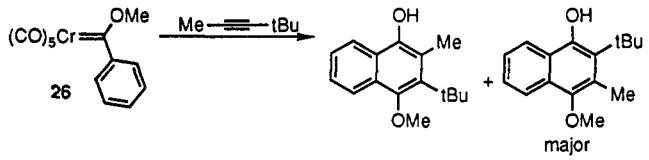
entry	compd	R_1	R_2	Y	X	M	ratio A:B	combined yield (%)
1	**18**	Et	Me	H	CF_3	Mo	50:50	77
2	**17**	tBu	Me	H	OMe	Mo	100:0	40
3	**19**	iPr	Me	H	H	Mo	72:28	35
4	**19**	iPr	Me	H	H	Cr	75:25	40
5	**20**	Ph	Me	H	H	Mo	95:5	44
6	**21**	Me	H	OMe	OMe	Mo	100:0	63
7	**22**	Et	Me	OMe	OMe	Mo	60:40	76
8	**23**	Et	Me	H	H	Mo	50:50	70

with two different groups on the cyclopropene double bond, the selectivity correlates with the steric size of the substituents, ranging from 100:0 for the competition of H vs Me (entry 6) to at best 60:40 with Me vs Et (entry 7). Good selectivity is observed (95:5) with Ph vs Me (entry 5), suggesting that more than steric parameters are important. In simplest terms, the regioselectivity is consistent with insertion of the metal into the cyclopropene single bond attached to the less crowded end of the cyclopropene double bond. The results parallel fairly quantitatively the degree of selectivity in the alkyne + carbene-metal process, considering unsymmetrical alkynes,[2] although the orientation is opposite. The electron-withdrawing trifluoromethyl group in **18** may be responsible for the fact that **18** rearranges approximately 10 times more slowly than **19**. Generally, the effect of arene substituent on rate is small; methoxy substitution (compare entries 2, 3, and 6) does not change the rate significantly.

It is noteworthy that the cyclopropene rearrangement leads to the opposite regioselectivity compared to the alkyne + carbene metal process (compare eqs 4 and 5).[2] The α-naphthols





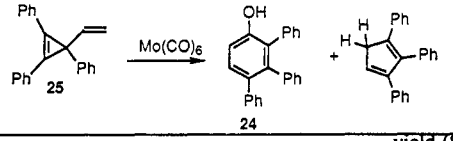


(5)

decomposed slowly on handling in solution, and the *O*-acetyl or *O*-methyl ether derivatives were usually prepared for the regioisomer assignment. In the case of the product from **17** (entry 2, Table 2), the methyl resonance for the aryl methyl and the acetyl methyl cannot be assigned directly by chemical shift analysis, and both were examined by nOe techniques. Irradiation of the *tert*-butyl signal resulted in signal enhancements of the upfield (δ 2.41) methyl signal and the aryl proton at C-4 (δ 7.62). Irradiation of the upfield methyl signal (δ 2.41) induced slight signal enhancement of the *tert*-butyl resonance. Therefore, the *tert*-butyl group is assigned to C-3 in the products from **17** (entry 2, Table 2).

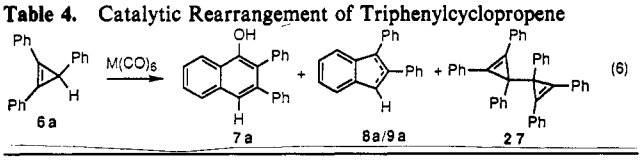
Metal-promoted rearrangement of simple vinyl cyclopropenes is also successful, giving rise to monocyclic phenols[24] (**24** from

Table 3. Rearrangement of 3-Vinylcyclopropene



conditions	yield (%)	
1,2-dimethoxyethane, 83 °C, 15 min	62	4
dioxane, 101 °C, 15 min	40	19

Table 4. Catalytic Rearrangement of Triphenylcyclopropene



entry	C_3Ph_3H	$MO(CO)_6$ (mol %)	conditions[a]	yield (%)[c] naphthol	indenes	dimer	SM
1	1.0 M	100	50 min[b]	78	11	0	0
2	1.0 M	33	12 h	73	16	0	0
3	1.0 M	25	19 h	70	19	0	0
4	0.25 M	10	1.7 h	46	30	0	22
5	neat	10	4.0 h	0	0	79	22
6	1.0 M	10	2.5 h	63	26	4	2
7	1.0 M	7	22 h	46	39	5	0
8	2.5 M	5	6.3 h	12	2	74	12
9	1.0 M	5	6.2 h	33	7	16	35
10	0.25	5	95.5 h	34	40	10	14

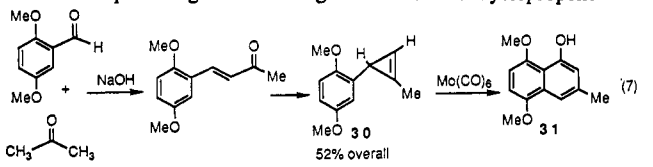
[a] Under 1.1 atm of CO. All other examples are under argon. [b] A cyclobuteneone was isolated in 7% yield (see text). [c] A cyclobuteneone was isolated in 17% yield (see text).

25, Table 3). Substrate **25** is the most reactive of the cases tested, giving complete conversion after 15 min in 1,2-dimethoxyethane at reflux (83 °C).[25]

In the general reaction of 3-phenylcyclopropenes with Cr and Mo hexacarbonyls, a significant amount of unreacted metal carbonyl was recovered at 100% conversion of the cyclopropene, suggesting less than a stoichiometric amount was required and some level of catalysis was operating, consistent with the expected mechanism (although added CO should be required). Table 4 and eq 6 display the results of a survey to develop the most efficient catalysis conditions. All reactions were carried out under about 1.1 atm of CO (balloon reservoir) in dioxane at reflux. As shown by entries 1–3, the reaction rate decreases as the amount of $Mo(CO)_6$ is decreased from 1.00 to 0.25 molar equiv, but the yield is only slightly diminished. The lower yield of naphthol is compensated by a rise in the yield of indene. As the concentration was increased in an effort to maintain high rates at lower temperatures, a new byproduct appears, the ene-coupling product, **27** (eq 6), typical reactivity of cyclopropenes in the absence of metals. This is most dramatic in the absence of solvent (entry 5), where the dimer **27** is produced in 100% yield at 78% conversion.

Benzannulation Approaches to Anthraquinone Antitumor Agents. A. Via Cyclopropene Rearrangements. An approach (Scheme 3) to anthraquinone antitumor agents such as 11-deoxydaunomycinone could make use of the cyclopropene rearrangement as a means of annulating a naphthalene derivative (**28**) into an anthraquinone (**29**). Several problems need to be addressed: (a) What is the efficiency and selectivity of rearrangement of a cyclopropene with one vinyl-H (as in **28**)? (b) How are the requisite naphthol-cyclopropenyl precursors prepared? (c) Can naphthols be benzannulated to anthracenes by the cyclopropene rearrangement? We were encourged in the last question by the corresponding results of Doetz, in which a carbene-metal + alkyne cycloaddition was reported to benzannulate a naphthalene system.[1b,16,17]

Table 5. Optimizing the Rearrangement of a 1-H Cyclopropene



entry	cyclopropene concentration (M)	$Mo(CO)_6$/ cyclopropene	reaction conditions[a]	% yield naphthol
1	0.25	1.2	dioxane, reflux	3
2	0.04	1.7	dioxane, reflux	13
3	0.025	1.0	3.3 mmol/min	28
4	0.025	2.0	7.0 mmol/min	42
5	0.025	2.0	8.4 mmol/min	40
6	0.029	2.2	12.0 mmol/min	37
7	0.025	10.0	3.4 mmol/min	40
8	0.030	2.0	8.0 mmol/min	63
9	0.026	10.0	1.4 mmol/min	55

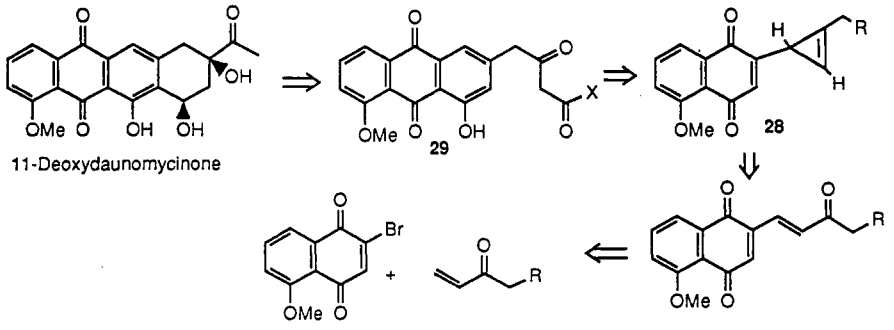
[a] Except for the first two entries, the cyclopropene in dioxane solution was added slowly by syringe pump to a mixture of the cyclopropene and the metal carbonyl.

The conditions for rearrangement of a monosubstituted cyclopropene were probed through study of **30**, prepared in three steps from acetone and 2,5-dimethoxybenzaldehyde, eq 7. Reaction of **30** with $Mo(CO)_6$ under standard conditions resulted in extensive polymerization and a low yield of the expected naphthol, **31**. A control experiment in the absence of metal carbonyl showed that polymerization reached 87% completion at 1 h in dioxane at reflux with a 0.025 M solution of the cyclopropene. The relative amount of polymer formation can be reduced by working at lower concentration, including slow addition of a solution of the cyclopropene to a heated mixture of the $Mo(CO)_6$. The relative amount of the metal carbonyl did not appear to be a significant factor. Only one regioisomer was observed, and the best yield obtained was 63% (entry 8, Table 5).

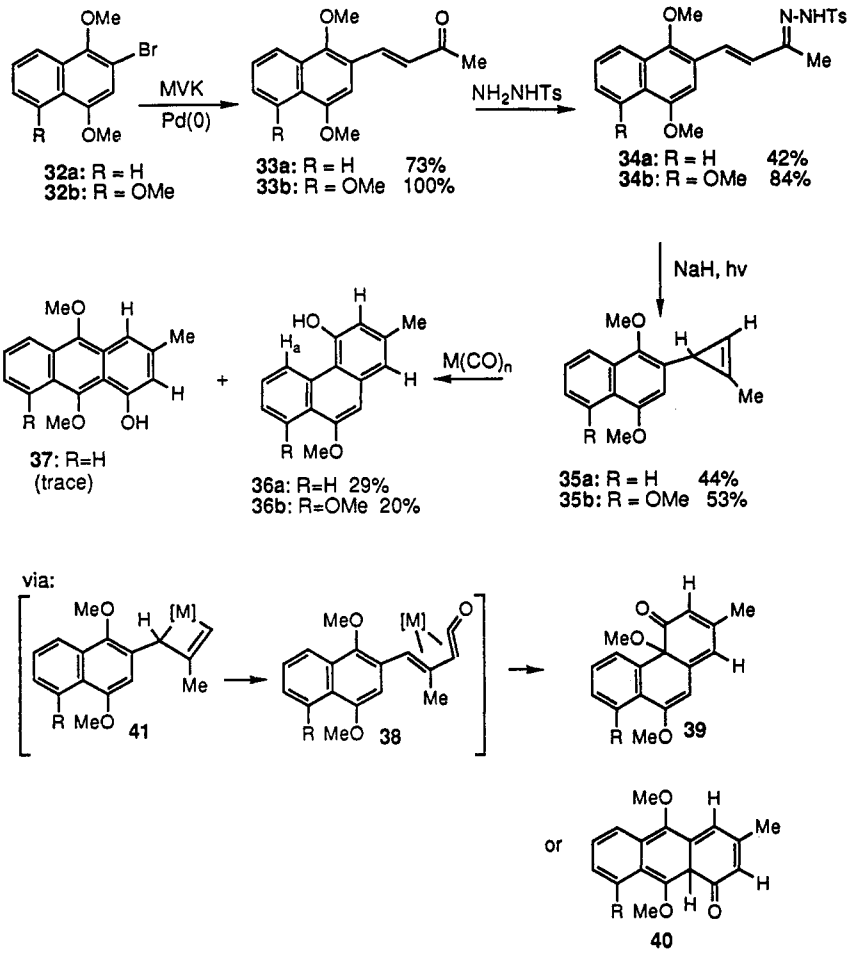
The preparation of the cyclopropenyl-substituted naphthalenes proceeded efficiently, according to Scheme 4. The Heck vinylation procedure[26] was very effective in attaching a vinyl ketone unit to the corresponding 2-bromonaphthalene (**32a**, **32b**). The final cyclopropyl formation proceeded in 44 and 53% yield for the two cases studied (**33a**, **33b**).

The attempted metal-promoted rearrangement of the cyclopropenes **35a** and **35b** led to a complex mixture from which the

Scheme 3. A Retrosynthesis for Anthraquinone Antibiotics

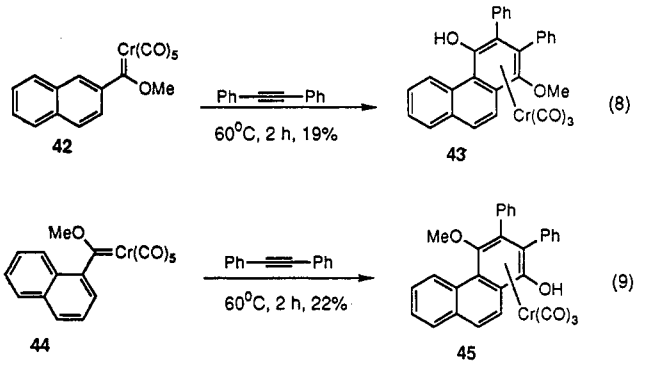


Scheme 4. Preparation and Reactions of Naphthylcyclopropenes



major product obtained in each case was identified as a phenanthrene, **36a** (29%) and **36b** (20%), Scheme 4. Although no anthracenes were isolated after extensive chromatography, a minor signal at δ 9.7 in the ^{1}H NMR spectrum of the crude product from **35a** could be attributed to the OH signal of the anthrol (**37**). The ratio of phenanthrol (**36a**) to anthrol (**37**) was >10:1 by integration of the ^{1}H NMR spectrum. The structure assignment for the phenanthrols is based heavily on the appearance of a characteristic signal at δ 9.2–9.6 (d, J = 8–9 Hz) for H_a in **36a** and **36b**, with all the other spectral data being consistent as well. The formation of phenanthrene structures to the exclusion of anthracenes is surprising because (a) it requires a replacement of an OMe group instead of H (unprecedented in the carbene–Cr benzannulation reactions) and (b) the corresponding carbene–chromium + alkyne reaction is reported to give anthracene derivatives. The formation of phenanthrenes presumably derives from cyclization of the vinylketene intermediate **38** onto the arene carbon bearing methoxy rather than onto the adjacent carbon bearing H.[25] This is understandable energetically on the basis of the calculation that the related phenanthrone **39** is more stable than the corresponding anthrone **40** by about 14 kcal/mol (comparing calculated heats of formation by AM1).[27]

The conversion of naphthalene derivatives to phenanthrenes via benzannulation with chromium carbene complexes (eqs 8 and 9) is well precedented in cases where the annulation replaces a hydrogen substituent on the naphthalene unit.[28] There is no previous example of replacement of a methoxy group during



benzannulation with chromium carbene complexes. For example, 2-naphthylchromium carbene complex **42** undergoes a benzannulation reaction with diphenylacetylene to give only phenanthrene complex **43**. Similarly, 1-naphthylchromium carbene complex **44** does undergo a benzannulation with diphenylacetylene at the β position of the naphthyl moiety to give **45**; cyclization to create an anthracene is not possible.

Non-metal-mediated electrocyclizations of vinylketenes onto the α positions of naphthalenes are also known. Heating cyclobutenone **46** produces a vinylketene (**47**) which, after electrocyclization and oxidation, gives only the angular product **48**, a result of electrocyclization to the α position of the naphthalene (eq 10).[29]

An especially relevant example is the thermolysis of 2-(1,4-dimethoxynaphthyl)cyclobutenone **49**, which after electrocy-

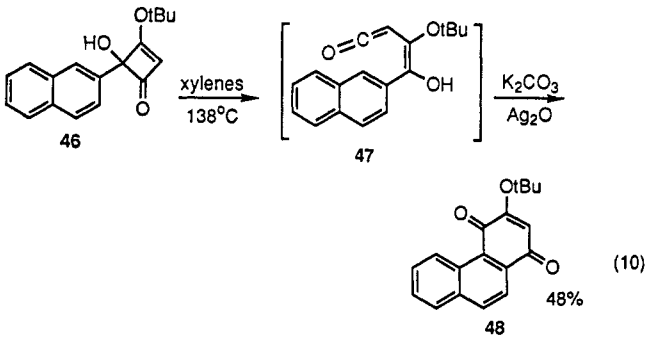
(25) Benzannulation via carbene–chromium complexes occurs faster toward a vinyl group compared to an aryl group. Doetz, K.-H.; Sturm, W. *J. Organomet. Chem.* **1985**, *285*, 205. We thank a referee for reminding us of this analogy.

(26) Heck, R. In *Comprehensive Organic Synthesis*; Trost, B., Fleming, I., Series Eds.; Pergamon: Oxford, 1991; Vol. 4, Chapter 4.3.

(27) For a presentation of the AM1 method, see: Dewar, M. J. S.; Zoebbisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

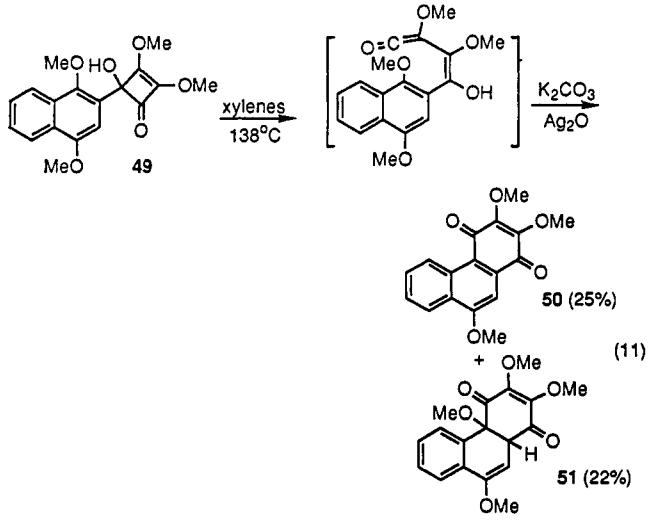
(28) Dötz, K. H.; Dietz, R. *Chem. Ber.* **1978**, *111*, 2517.

(29) Heerding, J. M.; Moore, H. W. *J. Org. Chem.* **1991**, *56*, 4048.



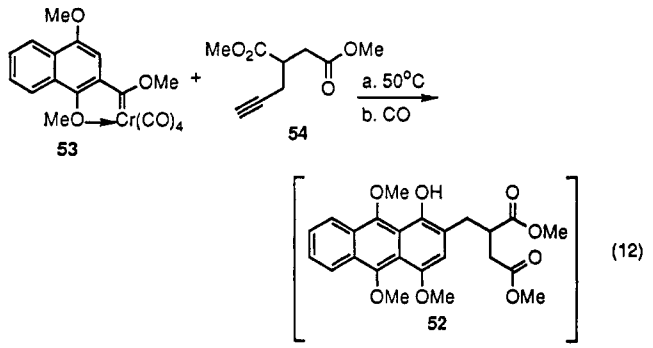
(10)

clization and oxidation gives only angular products **50** and **51**, even though the α position of the naphthalene is substituted with a methoxy group (eq 11).[30]



(11)

In the one reported example of benzannulation of a naphthalene derivative to an anthrahydroquinone (**52**) via a carbene–chromium complex (**53**) and alkyne **54** (eq 12), the positioning of a methoxy group was proposed as a blocking device.[1b,16,17] This process has been the subject of a patent.[17]



(12)

Because of the presumed mechanistic parallels but different product structures comparing the cyclopropene rearrangement process and the carbene–chromium benzannulation, and because a direct synthesis of anthraquinone from naphthalenes would be very useful, we have undertaken to check this result.[1b,16,17] On the basis of independent results in two laboratories, we find that the experimental data can be largely duplicated but that the structural assignment for **52** is not correct; the correct structure is the phenanthrene **56**.

The reagents for the benzannulation reaction of naphthylchromium carbene complex **53** and alkyne **54** were synthesized with some modifications of the published procedure.[1b] The benzannulation of naphthylchromium carbene complex **53** with alkyne **54** was carried out under the same conditions and using the same amounts of reagents/solvents reported[1b,17] Precipitation of the arene–$Cr(CO)_3$ complexes by addition of pentane to the dichloromethane solution proved incomplete. Lactone **55** was isolated from the precipitate after treatment with CO to detach the arene ligand (11% yield, Scheme 5). The filtrate was stirred in air at 22 °C for 1 h, and an additional sample of **55** (9% yield) was obtained by flash chromatography. The total yield of lactone **55** was 20% (403 mg). A series of minor byproducts were carefully separated, none in amounts more than 10 mg (<0.5% yield based on **55**) and none with spectral properties expected for the anthracene structure, such as **52** (see the Experimental Section).

Lactone **55** may be opened to phenol **56a** in 80% yield by stirring with excess $NaOCH_3$ in CH_3OH at room temperature. Conversely, **56a** can be partially converted back to **55** by drying under vacuum (0.01 mm) on silica gel at room temperature (**55** is produced in 74% yield and **56a** is recovered, 7%; monitored by ^1H NMR). This mixture was completely converted to **55** by stirring with *p*-TsOH·H_2O in benzene. Since phenol **56a** lactonizes to **55** on silica gel, it was considered that **56a** might be produced in the benzannulation reaction and cyclization to **55** occurs during chromatography. However, the 500-MHz ^1H NMR spectrum of the crude benzannulation/carbonylation reaction mixture prior to chromatography shows that only **55** is present. A simplified and slightly improved annulation procedure was developed to obtain phenol **56a** exclusively. By stirring the crude product with $NaOCH_3$ in CH_3OH for 2 h at 25 °C, lactone **55** is converted to phenol **56a** and the displacement of the Cr-$(CO)_3$ moiety from the crude product is made more complete. This method, which is operationally simpler and eliminates the use of a high-pressure $Cr(CO)_3$ decomplexation step with CO, produces **56a** in 29% yield. Alternatively, we find that acetylation *in situ* minimizes lactonization and produces **56b** in 45% yield after thorough chromatography.

A side by side comparison of the spectroscopic data assigned to **52** with that for **56a** reveals that the two sets of data are very similar and that the product is *almost certainly phenol* **56a** (Table 6). For phenol **52**, a 60-MHz ^1H NMR spectrum is reported containing three three-hydrogen singlets (δ 3.83, 3.92, and 3.98), a six-hydrogen methyl singlet (δ 3.71), in addition to a one-hydrogen singlet at δ 6.48, and two two-hydrogen doublets at $\sim\delta$ 7.5 and $\sim\delta$ 8.2. No phenol hydrogen signal is reported. In comparison, the more fully resolved 500-MHz ^1H NMR spectrum of **56a** shows four three-hydrogen methyl singlets (δ 3.65, 3.75, 3.95, 4.07), in addition to a one-hydrogen downfield doublet at δ 9.87 that is consistent only with an angularly fused phenanthrene.[31] This downfield signal is due to the bay region hydrogen of **56a** interacting with the electron cloud of the OH moiety (eq 12). In addition, the other aromatic proton signals, together with the δ 9.87 doublet, are consistent with structure **56a**, which requires two uncoupled aromatic hydrogens (δ 6.72 (s, 1H) and 7.38 (s, 1H)) and a four-hydrogen ABMX system (δ 7.55 (t, 1H), 7.60 (t, 1H), 8.32 (d, 1H), and 9.87 (d, 1H)). The phenol hydrogen of **56a** was determined to be the singlet at δ 7.79 by deuterium exchange.

The ^{13}C NMR of **56a** shows the required 23 carbon signals (7 aliphatic carbons (δ 39.8–56.1), 14 aromatic carbons (δ 95.6–153.3), and 2 carbonyl carbons (δ 173.1 and 176.1)). The ^{13}C NMR spectrum of **52**, which is not reported, would require 24 carbon signals. The infrared data for **56a** and **52** are quite similar. Both show OH stretching (3440 and 3660 cm^{-1}, respectively) and an ester carbonyl stretch (1740 and 1737 cm^{-1}, respectively). In addition, the IR spectrum of **56a** shows a strong carbonyl stretch at 1713 cm^{-1}, which is likely to be due to an ester moiety

(30) Moore, H. W.; Perri, S. T. *J. Org. Chem.* **1988**, *53*, 996.

(31) The hydrogen in the bay region of phenanthrene appears at δ 8.93, while the corresponding hydrogen signal in anthracene appears at δ 7.91. See: Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; John Wiley and Sons: New York, 1981; p 232.

Scheme 5. Phenanthrene Formation from Chromium–Carbene/Alkyne Cycloaddition

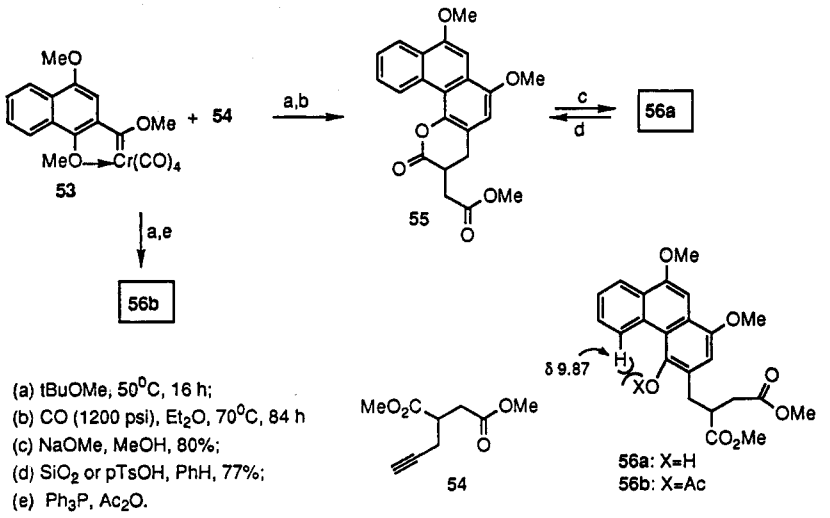


Table 6. Selected Spectral and Analytical Data for Phenol **52** and Phenol **56**

	52a	**56b**
^{1}H NMR	(60 MHz, $CDCl_3$) δ 3.71 (s, 6H), 3.83 (s, 3H), 3.92 (s, 3H), 3.98 (s, 3H), 6.48 (s, 1H), 7.37–7.72 (m, 2H), 8.09–8.43 (m, 2H)	(500 MHz, $CDCl_3$) δ 3.65 (s, 3H), 3.75 (s, 3H), 3.95 (s, 3H), 4.07 (s, 3H), 6.72 (s, 1H), 7.38 (s, 1H), 7.55 (t, 1H), 7.60 (t, 1H), 7.79 (s, 1H), 8.32 (d, 1H), 9.87 (d, 1H)
^{13}C NMR	not reported	(75 MHz, $CDCl_3$) 7 aliphatic carbons (δ 39.8–56.1), 14 aromatic carbons (δ 95.6–153.3), and 2-carbonyl carbons (δ 173.1 and 176.1)
IR	(KBr, cm^{-1}) 3440, 1740	(NaCl film, cm^{-1}) 3660 (w), 1737 (s), 1713 (s)
MS	*m/e* (% relative intensity) 442 (M^+, 38), 411 (27), 380 (100)	(EI) *m/e* (% relative intensity) 396 (M – 16, 5), 380 (M – CH_3OH, 30)
Anal.	C, 66.42; H, 5.96	C, 66.51; H, 6.00

[a] See refs 1b, 16, and 17. [b] This work. [c] Phenol **52** ($C_{24}H_{26}O_8$) requires C, 65.15; H, 5.92. Phenol **56a** ($C_{23}H_{24}O_7$) requires C, 66.98; H, 5.87.

which is intramolecularly hydrogen bonded to the phenol. The elemental analyses for **56a** and **52** are almost identical and are slightly low for the calculated analysis of phenol **56a** ($C_{23}H_{24}O_7$: C, 66.98; H, 5.87) but far off from the calculated values for **52**. The major difference in the spectral data of **52** and **56a** is in their mass spectra. A parent peak of 442 (38% relative intensity) is reported for **52**, while the highest molecular weight peaks for **56a** are seen at 396 (M –16, 5%) and 380 (M – CH_3OH, 30%). We cannot account for the discrepancy in these data.

Additional evidence for the structure of **56a** is based on the full characterization of lactone **55**. The 500-MHz ^{1}H NMR spectrum shows three three-hydrogen methyl singlets (δ 3.75, 4.00, and 4.09) and a downfield one-hydrogen doublet (δ 9.57), consistent with an angular phenanthrene structure.[27] Together with the δ 9.57 doublet, the other aromatic hydrogen signals are consistent with structure **55**, which requires two uncoupled aromatic hydrogens (δ 6.71 (s, 1 H) and 7.41 (s, 1H)) and a four-hydrogen ABMX system (δ 7.59 (t, 1H), 7.66 (t, 1H), 8.36 (d, 1H), and 9.57 (d, 1 H)). Other analytical data were also consistent. The structure of **55** was further supported by a single-crystal X-ray diffraction analysis, which confirms in all respects the proposed phenanthrene arrangement. The representation is shown in Figure 1. The results above show that there is as yet no procedure for the formation of anthraquinones via benzannulation with vinylcarbene–chromium intermediates, from either carbene + alkyne cycloaddition or cyclopropene rearrangement.

A likely mechanism which accounts for the formation of **55**/**56** in preference to **52** is shown in Scheme 6. The chelated methoxy group of carbene complex **53** initially dechelates, and the chromium coordinates an alkyne molecule to give **57**. Insertion of the alkyne gives vinylcarbene complex **58**, which inserts CO to form vinylketene **59**. This vinylketene may annulate onto one of two positions of the naphthalene moiety, at either an α position substituted with a methoxy group via **59a** or an unsubstituted β position via **59b**. Cyclization takes place onto the methoxy-

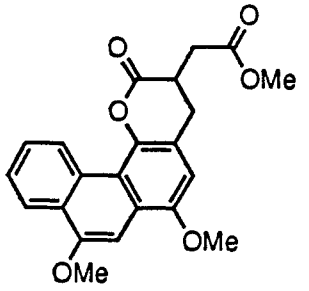


Figure 1. Representation for lactone **55**.

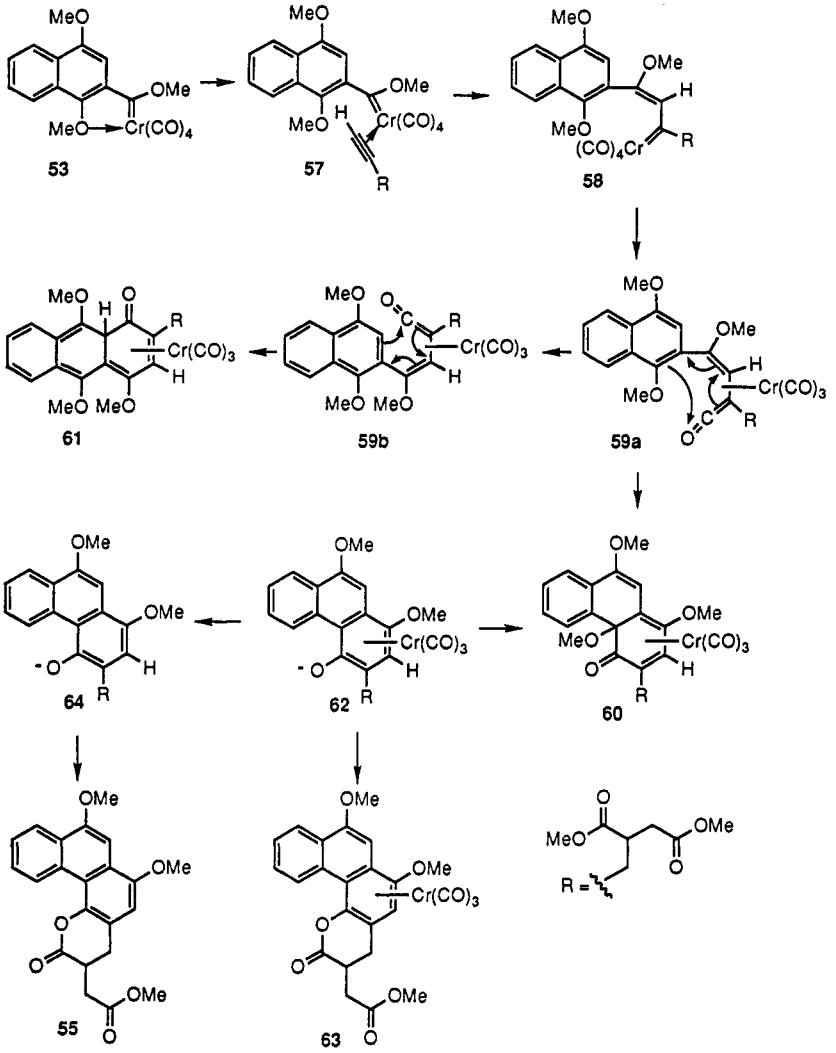
substituted α position to give **60** due to greater stability of **60** compared to **61** (recall calculations on **39**/**40**, above). Only intermediate **59b** may proceed to **61**, and this is not seen. Reduction of cyclohexadienone **60** with *in situ* generated Cr(0) may give complex **62**, which may either cyclize to lactone **63** or initially lose $Cr(CO)_3$ to give **64**, which then lactonizes to give **55**. Reduction of α-methoxy cyclohexadienone–$Cr(CO)_3$ complexes by Cr(0) has been seen previously in related systems.[32]

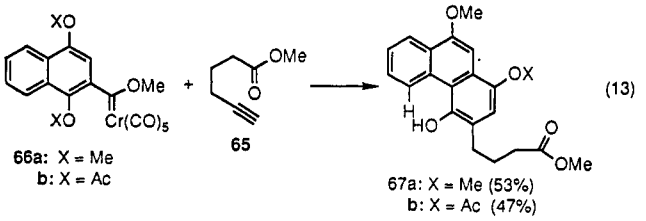
The analog (**65**) of alkyne **54** was allowed to react with both the naphthohydroquinone dimethyl ether carbene complex (**66a**) and the corresponding diacetoxy version, **66b**.[33] In each case, the predominant product is the phenanthrol (**67a** and **67b**). Among the minor products is a component tentatively identified as the regioisomer of **67a**, in which the alkyne has added with the opposite orientation. However, the quantities were small and the structure was not fully determined.

Alternative Precursors for the Naphthoquinone to Anthraquinone Conversion. Two alternatives were considered to circumvent the phenanthrone formation; the bis-ketal **68** and the naphthoquinone

(32) Wulff, W. D.; Kaesler, R. W.; Peterson, G. A.; Tang, P.-C. *J. Am. Chem. Soc.* **1985**, *107*, 1060.
(33) Semmelhack, M. F.; Lee, G. R. *J. Am. Chem. Soc.* **1987**, *6*, 1839.

Scheme 6. Proposed Mechanism of Phenanthrene Synthesis





69 were imagined to be derived from **35a** (Scheme 7). The preparation of **68** is based on the oxidations of Swenton,[34] converting a hydroquinone or quinone with a 2-bromo substituent into the enone and through the final cyclopropene synthesis. The monosubstituted cyclopropene **35a** is prone to polymerization, and the conditions of oxidation to give **68** required careful adjustment. Using a dual cell electrochemical apparatus with 1% KOH in methyl alcohol, a sample of the cyclopropene **35a** was electrolyzed at constant current (100 mA). The mixture was concentrated to about half volume without heating and then partitioned between water and dichloromethane. From the dichloromethane was isolated the bis-ketal **68** in >95% purity and 77% yield. It polymerized slowly at 25 °C and must be stored at low temperature. Perhaps due to this low stability, the metal-promoted rearrangement ($Cr(CO)_6$, $Mo(CO)_6$) failed to produce the desired anthraquinone, **70**.

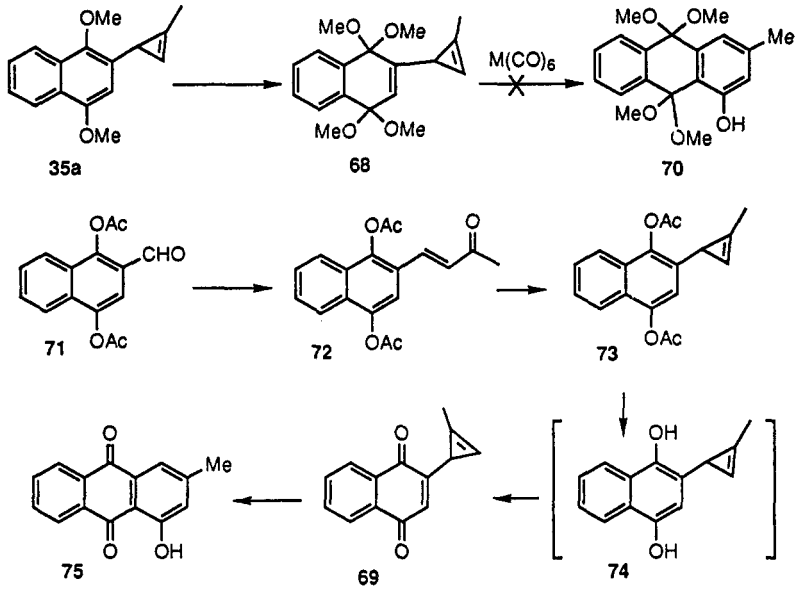
The quinone itself, **69**, offers an alternative, but no examples of 2-(3-cyclopropenyl)quinones have appeared in the literature. Direct hydrolysis of **68** failed, and several alternative precursors of **69** were prepared. The successful route involves the 2-formyl derivative, **71**, leading along the usual path via the enone **72** to the cyclopropene **73**. Deacylation of **73** was not successful under the usual hydrolytic conditions, but reduction with $LiAlH_4$ produced the hydroquinone (**74**), which spontaneously air-oxidized to **69**. The rearrangement of **69** to anthraquinone **75** was successful only with Mo carbonyl reagents, and then in yields under 20% (Scheme 7).[35] Polymerization of the cyclopropene under the reaction conditions seemed to be the major competing reaction, but even in the remarkably rapid reaction using $Mo(CO)_3(MeCN)_3$ in MeCN at 25 °C for 15 min, the yield of anthraquinone **75** was only 18%. While these experiments demonstrate one strategy for anthraquinone construction by benzannulation of naphthalene derivatives, in the present form it is not efficient.

Summary and Conclusions. Ring opening of 3-arylcyclopropenes with metal carbonyls of the chromium triad is a viable path to benzannulation products, presumably following the same pathway as the carbene–chromium/alkyne approach. The virtues of greater structural diversity available in the products as well as modest catalytic activity were shown with a series of simple cyclopropenes. High regioselectivity is observed, consistent with steric factors in the approach of the metal reagent to the two single bonds in the cyclopropene ring. The selectivity is generally

(34) Swenton, J. S.; Reynolds, P. W. *J. Am. Chem. Soc.* **1978**, *100*, 6188.

(35) The anthraquinone **72** is known: Jung, M. E.; Lowe, J. A.; Lyster, M. A.; Node, M.; Pfluger, R. W.; Brown, R. W. *Tetrahedron*, **1984**, 4751.

Scheme 7. Cyclopropenyulnaphthoquinone Derivatives



opposite of that observed with parallel substrates in the chromium–carbene/alkyne reaction. The conversion of 3-(2-naphthyl)cyclopropenes generates a phenanthrene skeleton instead of the expected anthracene structures. The apparent conflict with earlier reports of benzannulation of naphthalene derivatives to anthracenes via the chromium–carbene/alkyne reaction is resolved by reevaluation of the reported experimental observations and attempted duplication of the experiments. Alternative precursors for the naphthalene to anthracene conversion designed to avoid phenanthrene products were successful, but of too low efficiency to be considered useful methodology.

Experimental Section

General. Proton (^{1}H) NMR spectra were recorded on a General Electric QE-300 (300 MHz) or a JEOL GSX 270 (270 MHz). Proton chemical shifts, reported in parts per million, were referenced to tetramethylsilane either directly as an internal reference or indirectly by employing known resonances due to trace protio-solvent. Coupling constants (J) are reported in Hertz (Hz). Multiplicities are abbreviated: singlet s, doublet d, triplet t, quartet q, multiplet m. Carbon-13 (^{13}C) NMR spectra were recorded on a General Electric QE-300 (75.4 MHz) or a JEOL GSX 270 (67.9 MHz). Carbon-13 chemical shifts were indirectly referenced to tetramethylsilane by employing known solvent ^{13}C resonances as internal references. Infrared (IR) spectra were recorded on a Digilab FTS-20c or a Nicolet 730 FT-IR spectrometer with internal calibration. Mass spectral data were obtained using a Kratos MS 50TC-RFA spectrometer operating in electron impact mode at 70 eV, unless otherwise noted. Peaks are indentified by mass/charge (m/e) and relative abundance to base peak (%). Flash column chromatography was performed using Merck Silica 60 (230-400 mesh) according to the procedure of Still. Analytical thin layer chromatography (TLC) was conducted on Machery-Nagel SIL G/UV254 plastic-backed silica gel plates. Developed plates were visualized with an Ultraviolet Light Products lamp UVS-11, stained with 1% p-anisaldehyde solution or 2% phosphomolybdic acid solution and heated. Melting points are uncorrected and were recorded on an Electrothermal melting point apparatus # IA6304 using open capillary tubes.

Anhydrous diethyl ether, tetrahydrofuran (THF), and 1,2-dimethoxyethane (DME) were obtained by distillation from sodium benzophenone ketyl. Benzene and toluene were dried azeotropically by simple distillation; after ~10% of the initial volume was distilled and discarded the pure solvent was collected. Dichloromethane and acetonitrile were distilled from CaH_2. N,N-Dimethylformamide (DMF) was stored over activated molecular sieves several days prior to use or distilled from calcium hydride at reduced pressure. Hexane for column chromatography was purified by simple distillation. Pyridine, triethylamine, and diisopropylamine were distilled from KOH. All other solvents were ACS grade and were used without further purification. Commercial reagents were used without further purification. All reagents were purchased from Aldrich Chemical Co. unless otherwise noted. Copper iodide was purified according to a literature procedure.[36] Alkyl lithium solutions were obtained as solutions in hexane and their concentrations determined using diphenylacetic acid.[37] Operations with air-sensitive compounds were performed under argon using double-manifold techniques.[38]

Table 1. Rearrangement of 3-Substituted 1,2,3-Triphenylcyclopropenes (6) with $Cr(CO)_6$. A mixture of the cyclopropene 6[18,19] (0.5 mmol) and 2.0 molar equiv of $Cr(CO)_6$ in di(n-butyl) ether was heated at reflux under argon for the time indicated in Table 1. The reaction was monitored by disappearance of starting cyclopropene by TLC. After the desired reaction period, the solvent was removed under vacuum and the residue was O-methylated or O-acylated to facilitate purification.

Methylation involved adding the crude α-naphthol to a two-phase mixture (1:1 CH_2Cl_2:water) containing 2–3 molar equiv of methyl iodide, 1.0 molar equiv of benzyltriethylammonium iodide, and 1.5 molar equiv of NaOH. After the mixture was stirred overnight at 25 °C, the organic layer was separated and the aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were washed with dilute aqueous NaOH solution, dried, and concentrated, and the residue was purified by flash chromatography (silica gel; hexane:ethyl acetate, 19:1).

Acetylation involved adding the crude α-naphthol to a mixture of acetic anhydride (2 molar equiv) and DMAP (1.5 molar equiv) in CH_2Cl_2 at 25 °C for 3 h. The mixture was diluted with ether, and the resulting solution was washed with dilute aqueous HCl, dried, and concentrated. The residue was purified by flash chromatography (silica gel; hexane: ethyl acetate, 19:1).

Rearrangement of 3-Substituted 1,2,3-Triphenylcyclopropenes (6) with $Mo(CO)_6$. Exactly as above, but using dioxane as solvent at reflux, a mixture of naphthol and indenes was obtained. The naphthol was separated from the indenes by flash chromatography (hexane, then hexane/ethyl acetate), and the indenes were characterized as a mixture of two alkene isomers. The naphthol fraction was treated with acetic anhydride as above, and the O-acetate was characterized.

Characterization of 4-Methyl-2,3-diphenyl-1-naphthalenol (7, R = Me). Recrystallized from ethanol: mp 202–205 °C. IR(CCl_4): 3560 cm^{-1} (OH). ^{1}H NMR ($CDCl_3$): δ 2.39 (s, 3H), 5.32 (s, 1H), 6.98–7.26 (m, 10H), 7.55 (m, 2H), 8.05 (d, 1H, J = 9 Hz), 8.32 (d, 1H, J = 9 Hz). ^{13}C NMR ($CDCl_3$): δ 16.41, 122.06, 123.00, 123.52, 123.61, 124.52, 125.25, 126.30, 126.88, 127.56, 127.70, 128.88, 130.55, 131.29, 133.12, 135.86, 138.95, 141.01, 146.46. MS (EI): 310 (M^+, 100), 289 (3.4), 278 (2.6), 265 (3.4), 231 (2.7), 202 (3.9). Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 88.85; H, 5.83.

Characterization of 4-Ethyl-2,3-diphenyl-1-naphthalenol (7, R = Et). Recrystallized from hexane: mp 163–165 °C. IR ($CDCl_3$): 3550 (OH), 1594, 1498, 1391 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.21 (t, 3H, J = 7 Hz),

(36) Kaufman, G. *Inorg. Synyh.* **1983**, *22*, 101.
(37) Kofon, W. G.; Baclawski, L. M. *J. Org. Chem.*, **1976**, *41*, 1879.
(38) Shriver, D. F. *The Manipulation of Air-sensitive Compounds*; McGraw-Hill: New York, 1969.

2.89 (q, 2H, J = 7 Hz), 5.36 (s, 1H), 7.08–7.29 (m, 10H), 7.55–7.65 (m, 2H), 8.15 (d, 1H, J = 8 Hz), 8.41 (d, 1H, J = 1 Hz). ^{13}C NMR ($CDCl_3$): δ 15.88, 22.70, 121.96, 123.04, 123.79, 124.35, 124.99, 126.17, 126.68, 127.33, 127.41, 128.67, 129.85, 130.07, 131.13, 131.90, 135.63, 138.50, 140.66, 146.27. MS (EI): 325 (30), 324 (M^+, 100), 309 (28), 290 (15), 289 (20) , 231 (7.1), 202 (8.4), 138 (11). Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.61; H, 6.26.

Characterization of 3-ethyl-1,2-diphenylindene (8, R = Et): recrystallized from methanol, mp 140–141 °C. IR ($CDCl_3$): 3070, 3030, 2980, 2940, 2880, 1601, 1493, 1466, 1454, 1373, 1335 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.39 (t, 3H, J = 8 Hz), 2.76 (dq, 2H, J = 8, 1 Hz), 4.95 (broad s, 1H), 7.03–7.45 (m, 14H). ^{13}C NMR ($CDCl_3$): δ 13.97, 19.37, 58.04, 119.50, 123.83, 125.26, 126.43, 126.63, 126.75, 128.11, 128.44, 128.78, 136.43, 139.86, 141.66, 144.63, 144.84, 148.43. MS (EI): 296 (M^+, 89), 267 (100), 202 (14), 170 (11), 136 (16), 132 (38), 129 (41), 69 (26). Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.07; H, 6.88.

Characterization of 2,3-Diphenyl-1-methoxy-4-(1-methylethyl)naphthalene (7, R = iPr; OMe Ether). Recryallized from hexane: mp 129–130 °C; IR($CDCl_3$): 3063, 3016, 2959, 2931, 2843, 1582, 1497, 1443, 1370, 1350, 1273, 1215, 1122, 1069, 1030 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.52 (d, 6H, J = 7 Hz), 3.42 (m, 1H), 3.55 (s, 3H), 7.02–7.22 (m, 10H), 7.57 (m, 2H), 8.32 (m, 1H), 8.46 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 22.55, 31.29, 61.22, 123.38, 125.28, 125.96, 126.06, 126.59, 127.12, 127.33, 128.50, 130.04, 130.68, 131.38, 132.05, 137.47, 137.90, 139.67, 141.30, 151.44. MS (EI): 353 (28), 352 (M^+, 100), 337 (38), 323 (20), 322 (76), 307 (46), 305 (30), 289 (20). Exact mass calcd for $C_{26}H_{24}O$: 352.1827. Found: 352.1830.

Characterization of 3-(1-methylethyl)-1,2-diphenylindene (8, R = iPr): recrystallized from methanol, mp 103–104 °C. IR ($CDCl_3$): 3060, 3024, 2966, 2931, 2874, 1597, 1493, 1466, 1385, 1366, 1153, 1123, 1072, 1303 cm^{-1}. ^{1}H NMR($CDCl_3$): δ 1.33 (d, 3H, J = 7 Hz), 1.48 (d, 3H, J = 7 Hz), 3.26 (pseudo septet, 1H, J = 7 Hz), 4.80 (2, 1H), 6.93 (d, 1H, J = 8 Hz), 7.06–7.29 (m, 7H), 7.61 (d, 1H, J = 8 Hz). ^{13}C NMR ($CDCl_3$): δ 21.06, 21.67, 27.23, 58.73, 121.52, 124.19, 124.88, 126.37, 126.41, 126.65, 127.91, 128.20, 128.36, 129.13, 137.05, 139.74, 143.52, 144.82, 145.06, 149.15. MS (EI): 310 (M^+, 37), 268 (30), 267 (100), 265 (13), 252 (5.8), 215 (3.2). Anal. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.57; H, 7.21.

Characterization of 4-Ethyl-2,3,4-triphenyl-2-cyclobuten-1-one (10, R = Et). Recrystallized from hexane: mp 36–39 °C. IR (hexane): 1763 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 1.04 (t, 3H, J = 7 Hz), 2.26 (dq, 1H, J = 14, 7 Hz), 2.57 (dq, 1H, J = 14, 7 Hz), 7.20–7.49 (m, 11H), 7.62 (d, 2H, J = 8 Hz), 7.75 (d, 2H, J = 8 Hz). ^{13}C NMR ($CDCl_3$): δ 10.21, 24.33, 74.66, 126.48, 127.11, 127.85, 128.59, 128.64, 128.73, 128.95, 129.09, 129.36, 131.23, 131.98, 140.23, 143.65, 166.55, 191.98. MS (EI): 324 (M^+, 34), 309 (37), 296 (18), 268 (24), 267 (100), 265 (30), 252 (19), 203 (29), 202 (24), 170 (38). HRMS calcd for $C_{24}H_{20}O$: 324.1514. Found: 324.1520.

Characterization of 4-(1-Methylethyl)-2,3,4-triphenyl-2-cyclobuten-1-one (10, R = iPr). IR (hexane): 1758 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 1.15 (d, 3H, J = 7 Hz), 1.18 (d, 3H, J = 7 Hz), 2.89 (pseudo septet, 1H, J = 7 Hz), 7.03–7.74 (m, 15H). ^{13}C NMR ($CDCl_3$): δ 19.56, 19.83, 30.59, 79.03, 126.97, 127.16, 127.71, 128.39, 128.48, 128.64, 128.76, 128.98, 129.19, 130.75, 132.86, 139.81, 143.07, 169.43, 192.81. MS (EI): 338 (M^+, 22), 324 (38), 323 (90), 295 (11), 268 (35), 267 (90), 265 (27), 178 (20), 165 (25), 105 (78), 91 (34), 85 (91), 83 (100). HRMS calcd for $C_{25}H_{22}O$: 338.1671. Found: 338.1670.

Typical Conversion of Tosylhydrazones to Cyclopropenes: Preparation of 1-Methyl-2-isopropyl-3-phenylcyclopropene, 19. A suspension of the corresponding tosylhydrazone (0.324 g, 1.0 mmol), sodium hydride (0.060 g, 2.5 mmol), and pentane/diglyme (60 mL, 9:1 v/v) was irradiated (450-W Hg arc; Pyrex filter) with bubbling of argon through the mixture for 10 min. The precipitate was filtered and the filtrate washed 10 times with distilled water and then dried over sodium sulfate. After removal of the solvent, the yellow liquid residue was separated by column chromatography using 10% ethyl acetate in hexane as the eluent. The cyclopropene **19**, a colorless liquid, was obtained (0.080 g, 47% yield, R_f (10% ethyl acetate in hexane, SiO_2) = 0.63). ^{1}H NMR ($CDCl_3$): δ 1.15 (dd, 6H, J = 3, 7 Hz, H at C-1, C-3), 2.1 (s, 3H, H at C-6), 2.5 (s, 1H, H at C-7), 2.8 (m, 1H, H at C-2), 7.2 (m, 5H, H at Ph). IR ($CDCl_3$): 3000–2850, 1500–1420, 890, 780–670, 640 cm^{-1}. MS: 172 (parent, 12.8), 148 (42.7), 147 (30.5), 120 (37.4), 105 (100), 104 (24.8), 91 (40.8), 83 (20.7), 78 (36.2), 77 (63.0). HRMS calcd for $C_{13}H_{16}$: 172.2725. Found: 172.1237.

Characterization of 1-(1,1-Dimethylethyl)-2-methyl-3-(4-methoxyphenyl)cyclopropene, 17. IR ($CDCl_3$): 2962, 2900, 2866, 1609, 1508, 1458, 1443, 1277, 1242, 1173, 1038, 914, 899, 837 cm^{-1}. ^{1}H NMR ($CDCl_3$)-SPCLN δ 1.08 (s, 9H), 2.01 (s, 9H), 2.39 (s, 1H), 3.73 (s, 3H), 6.74, 6.96 (d, AA'BB', 2H, 2H). ^{13}C NMR ($CDCl_3$): δ 8.70, 24.76, 28.68, 31.74, 55.25, 103.37, 113.36, 119.88, 125.99, 139.94, 156.99. MS (EI): 216 (M^+, 9.0), 201 (28), 186 (57), 171 (16), 160 (100), 159 (60), 145 (31). HRMS calcd for $C_{15}H_{20}O$: 216.1514. Found: 216.1521.

Characterization of 1-Methyl-2-ethyl-3-(*p*-(trifluoromethyl)phenyl)-cyclopropene, 18. The crude product was filtered through silica gel and concentrated, separated by column chromatography (eluting with 10% ethyl acetate in hexane), and flash distilled at 25 °C/0.07 mm to yield pure cyclopropene (0.177 g, 31.3% yield). ^{1}H NMR ($CDCl_3$): δ 1.2 (3H, t, J = 7 Hz, H at C-1), 2.1 (3H, d, J = 1 Hz, H at C-5), 2.45 (2H, m, J = 7 Hz, H at C-2), 2.49 (1H, s), 7.15 (2H, d, J = 8 Hz), 7.5 (2H, d, J = 8 Hz) ppm; ^{13}C NMR($CDCl_3$): 9.10, 12.10, 17.97, 105.42, 111.73, 124.95, 125.48, 152.49. IR ($CHCl_3$): 3050–2850 (br), 1620, 1320, 1160, 1120, 1060, 1010, 840, 780–700 cm^{-1}. MS: 226 (parent, 8.7), 212 (13.2), 211 (100), 197 (20.9), 196 (16.6), 191 (36.8), 183 (26.8), 142 (37.9), 141 (17.8), 128 (24.4). HRMS calcd for $C_{13}H_{13}F_3$: 226.0969. Found: 226.0970.

Characterization of 3-(2,5-Dimethoxyphenyl)-1-methylcyclopropene, 21. IR ($CDCl_3$): 2997, 2943, 2909, 2835, 1605, 1585, 1497, 1466, 1277, 1242, 1215, 1177, 1161, 1049 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.20 (s, 3H), 2.91 (d, J = 2 Hz, 1H), 3.78 (s, 3H), 3.86 (s, 3H), 6.40 (d, J = 3 Hz, 1H), 6.59 (br s, 1H), 6.66 (dd, J = 8, 3 Hz, 1H), 6.83 (d, J = 8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 10.38, 16.08, 55.47, 56.50, 98.61, 109.57, 111.85, 111.94, 116.16, 137.04, 152.79, 153.87. MS (EI): 190 (M^+, 48), 175 (100), 160 (22), 147 (28), 132 (42), 115 (45), 103 (21), 91 (23), 78 (43). HRMS calcd for $C_{12}H_{14}O_2$: 190.0994. Found: 190.1001.

Characterization of 1-Methyl-2-ethyl-3-(2,5-dimethoxyphenyl)cyclopropene, 22. Cyclopropene **22** (0.363 g, 33% yield) was obtained. ^{1}H NMR ($CDCl_3$): δ 1.18 (t, 3H, J = 7 Hz, H at C-5), 2.08 (s, 3H, H at C-1), 2.45 (m, 2H, H at C-4), 2.78 (s, 1H, H at C-6), 3.76 (s, 3H), 3.83 (s, 3H), 6.4 (d, 1H, J = 2 Hz), 6.6 (dd, 1H, J = 2 Hz, 10 Hz), 6.8 (d, 1H J = 10 Hz). ^{13}C NMR ($CDCl_3$): δ 9.4, 12.3, 18.2, 18.5, 55.7, 56.8, 105.2, 108.8, 111.5, 111.9, 112.3, 137.9, 153.0, 154.05. IR ($CDCl_3$): 3050–2820, 2815, 1490 and 1460 (Ph), 1270, 1210, 1170, 1045 cm^{-1}. MS: 218 (parent, 65), 203 (100), 189 (97.3), 188 (40.8), 173 (46.7), 172 (30.9), 159 (34.0), 115 (24.6), 91 (40.0), 78 (33.2). Anal. Found: C, 77.34; H, 8.62. Calcd for $C_{14}H_{18}O_2$: C, 77.01; H, 8.33.

Characterization of 1-Methyl-2-ethyl-3-phenylcyclopropene, 23. The crude cyclopropene **23** was purified by flash chromatography (eluting with hexane) and flash distillation (30 °C/0.07 mm) to yield pure **23** as a clear liquid. ^{1}H NMR ($CDCl_3$): δ 1.15 (t, 3H, J = 7 Hz, H at C-1), 2.1 (s, 3H, H at C-5), 2.45 (d, 1H, J = 2 Hz, H at C-6), 2.45 (m, 2H, H at C-2), 7.1 (m, 3H), 7.25 (d, 2H, J = 7 Hz). ^{13}C NMR ($CDCl_3$): δ 9.23, 12.24, 18.07, 25.6, 106.05, 112.34, 124.8, 125.45, 128.07, 147.91. IR ($CDCl_3$): 3100–2800, 1880, 1820–1790, 1600, 1500–1430, 1380, 1210, 1090, 990 cm^{-1}. MS: 158 (parent, 15.9), 145 (12.4), 143 (100), 142 (12.7), 141 (15.1), 129 (44.6), 128 (91.0), 127 (23.2), 115 (22.5), 77 (14.3). HRMS found: 158.1097. Calcd for $C_{12}H_{14}$: 158.1095.

Typical Procedure for Cyclopropene Rearrangements in Table 2. Table 2, Entry 3. Rearrangement of Cyclopropene 19 with $Mo(CO)_6$. A mixture of cyclopropene **19** (0.172 g, 1.0 mmol), molybdenum hexacarbonyl (Aldrich, sublimed, 0.317 g, 1.2 mmol), and 4.0 mL of dioxane was heated at reflux for 3 h. As the mixture was heated, the molybdenum hexacarbonyl dissolved and the solution turned green; the reaction was monitored by TLC. The reaction mixture was then cooled to 23 °C, diluted with ether, and allowed to stir in air for 15 min. It was then filtered through Celite, the solvent was removed at reduced pressure, and the precipitated molybdenum hexacarbonyl was filtered. The crude product was separated by flash chromatography using 400 mL of 25% hexane in benzene as the eluent. The two isomeric products (0.052 g, 25% yield; 0.021 g, 10% yield) were thus obtained. Major isomer, ^{1}H NMR ($CDCl_3$): δ 1.35 (d, 6H, J = 7 Hz, H at C-1, C-3), 2.4 (s, 3H, H at C-6), 3.3 (m, 1H, H at C-2), 5.1 (s, 1H, OH), 7.4 (m, 3H), 7.77 (m, 1H), 8.05 (m, 1H) ppm. Minor isomer, ^{1}H NMR ($CDCl_3$): δ 1.5 (d, 6H, J = 7 Hz, H at C-1, C-3), 2.5 (s, 3H, H at C-6), 3.5 (m, 1H, H at C-2), 5.3 (s, 1H at OH), 7.3 (d, 1H, J = 1 Hz), 7.4 (m, 2H), 7.7 (m, 1H), 8.0 (m, 1H). Data on the mixture, IR ($CHCl_3$): 3600–3200 (OH), 3100–2800, 1650, 1590, 1450, 1280, 900 cm^{-1}. MS: 200 (parent, 89.2), 199 (15.2), 186 (21.7), 185 (100), 171 (17.9), 170 (18.3), 157 (13.8), 128 (14.5).

The major isomer was fully characterized as the methyl ether. ^{1}H NMR ($CDCl_3$): δ 1.35 (d, 6H, J = 7 Hz, H at C-1, C-3), 2.5 (s, 3H, H at C-6), 3.3 (m, 1H, H at C-2), 3.9 (s, 3H), 7.45 (m, 2H), 7.5 (s, 1H, H at C-14), 7.8 (m, 1H), 8.05 (m, 1H). NOE measurements showed enhancement of H at C-6 and C-14 upon irradiation of H at C-1 and C-3; of H at C-1, C-3, and C-15 upon irradiation of H at C-6; and of H at C-6 upon irradiation of H at C-15. ^{13}C NMR ($CDCl_3$): δ 11.73, 23.7, 29.9, 61.4, 119.3, 121.9, 125.2, 125.4, 125.6, 126.4, 127.7, 133.4, 146.9, 153.6. MS: 214 (parent, 91.4), 199 (100), 184 (28.9), 180 (18.7), 171 (20.9), 153 (15.0), 151 (14.4), 141, 23.5, 128 (18.3), 115 (16.4). Anal. Calcd for $C_{15}H_{18}O$: C, 84.05; H, 8.48. Found: C, 83.85; H, 8.55.

Table 2, Entry 4. Rearrangement of Cyclopropene 19 with $Cr(CO)_6$. A mixture of cyclopropene (106 mg, 0.62 mmol), chromium hexacarbonyl (273 mg, 1.24 mmol), and 2.5 mL of *n*-butyl ether was heated at reflux; upon heating, the solution turned brown. After 3 h, the reaction mixture was cooled and the solvent removed under vacuum. Pyridine (2.5 mL) was then added and the mixture again heated at reflux for 4 h, after which the solvent was again removed under vacuum at 23 °C. The crude mixture was diluted with ether, filtered through silica gel, and concentrated to yield the crude product, which was then loaded onto four 250-micron prep chromatography plates and eluted with 5% ethyl acetate in hexane. The separation yielded a product identical with the major isomer from the $Mo(CO)_6$ procedure above (38 mg, 30% yield) and a second product identical with the minor isomer from $Mo(CO)_6$ (13 mg, 10% yield).

Table 2, Entry 1. Characterization of 2-Methyl-3-ethyl-7-trifluoromethylnaphthol and 2-Ethyl-3-methyl-7-(trifluoromethyl)naphthol. The crude product was separated by flash chromatography, eluting with 20% ethyl acetate in hexane. The column yielded two isomers separately in a ratio of about 1:1. The total yield of naphthols was 112.6 mg, 77%.

Isomer A (2-Methyl-3-ethyl-7-(trifluoromethyl)naphthol): mp 90–91 °C. ^{1}H NMR ($CDCl_3$): δ 1.3 (t, 3H, J = 8 Hz), 2.4 (s, 3H), 2.85 (q, 2H, J = Hz), 5.17 (s, 1H, OH), 7.34 (s, 1H), 7.6 (d, 1H, J = 8 Hz), 7.8 (d, 1H, J = 8 Hz), 8.45 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 11.44, 14.61, 27.47, 117.19, 118.66, 119.60, 121.22, 122.0, 126.5, 127.0, 128.09, 134.00, 144.27, 149.42.

Isomer B (2-ethyl-3-methyl-7-(trifluoromethyl)naphthol): ^{1}H NMR ($CDCl_3$) δ 1.25 (t, 3H, J = 8 Hz), 2.5 (s, 3H), 2.85 (q, 2H, J = 8 Hz), 5.24 (s, 1H, OH), 7.32 (s, 1H), 7.55 (dd, 1H, J = 1, 9 Hz), 7.8 (d, 1H, J = 9 Hz), 8.45 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 13.60, 19.82, 20.49, 105.07, 109.40, 119.70, 120.74, 121.3, 123.0, 124.0, 127.87, 134.0, 137.90. MS (on a mixture of isomers): 254(parent, 16.7), 253 (100), 239 (11.0), 238 (16.9), 210 (9.0), 190 (11.5), 149 (9.5), 141 (7.0). Anal (on a mixture of isomers). Calcd for $C_{14}H_{13}OF_3$: C, 66.14; H, 5.15. Found: C, 65.72; H, 5.08.

Table 2, Entry 2. Characterization of 3-(1,1,-Dimethylethyl)-7-methoxy-2-methyl-1-naphthalenol, Acetate. Following the general procedure with cyclopropene **17** (Table 2), including acetylation of the crude naphthol, the acetate was obtained as a colorless solid and recrystallized from hexane: mp 93–94 °C. IR (CCl_4): 1771 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.45 (s, 9H), 2.41 (s, 3H), 2.44 (s, 3H), 3.84 (s, 3H), 6.84 (d, 1H, J = 2 Hz), 7.03 (dd, 1H, J = 9, 2 Hz), 7.62 (s, 1H), 7.64 (d, 1H, J = 9 Hz). ^{13}C NMR ($CDCl_3$): δ 15.54, 20.82, 31.39, 36.18, 55.36, 99.13, 118.21, 122.55, 126.26, 127.16, 127.97, 129.86, 144.53, 145.24, 158.17, 169.15. MS (EI): 286 (M$^+$, 30), 244 (100), 229 (53), 188 (7.1), 115 (5.0). Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.50; H, 7.74. Found: C, 75.43; H, 7.77.

Table 2, Entry 5. Characterization of 1-Methoxy-2-methyl-3-phenylnaphthalene. Following the general procedure with cyclopropene **20** (Table 2), including methylation, the *O*-methyl ether was obtained as a colorless solid, recrystallized from hexane: mp 79–81 °C. IR (CCl_4): 1367, 1156, 1105 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.36 (s, 3H), 3.98 (s, 3H), 7.55 (s, 1H), 7.40–7.52 (m, 7H), 7.82 (d, 1H, J = 8 Hz), 8.14 (d, 1H, J = 8 Hz). ^{13}C NMR ($CDCl_3$): δ 13.92, 61.11, 121.78, 124.42, 125.10, 125.65, 125.79, 126.95, 127.05, 127.88, 128.04, 129.31, 132.87, 141.68, 141.91, 153.81. MS(EI): 248 (M$^+$, 100), 233 (16), 215 (20), 202 (13), 189 (4.8), 178 (3.3). Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 87.39; H, 6.88.

Characterization of 1-methoxy-3-methyl-2-phenylnaphthalene: colorless solid; not recrystallized. IR (CCl_4): 1366, 1088 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.22 (d, 3H, J = 1 Hz), 3.53 (s, 3H), 7.31–7.49 (m, 7H), 7.51 (s, 1H), 7.78 (m, 1H), 8.09 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 21.32, 61.43, 122.38, 123.69, 125.22, 126.23, 126.53, 126.98, 127.13, 128.15, 129.94, 132.26, 134.11, 135.45, 137.55, 153.15. MS (EI): 249 (19), 248 (M$^+$, 100), 233 (41), 218 (56), 205 (16), 202 (14), 101 (11). HRMS Calcd for $C_{18}H_{16}O$: 248.1201. Found: 248.1192.

Table 2, Entry 6. Characterization of 5,8-Dimethoxy-3-methyl-1-naphthalenol. Following the general procedure with cyclopropene **22** (Table 2), including methylation, the *O*-methyl ether was obtained as a colorless solid and recrystallized from hexane: mp 118–121 °C. IR ($CDCl_3$): 3387, 3017, 2955, 2939, 1639, 1616, 1516, 1431, 1389, 1277, 1250, 1215, 1092, 1057 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.44 (s, 3H), 3.93 (s, 3H), 4.00 (s, 3H), 6.05 (m, 2H), 6.77 (s, 1H), 7.49 (s, 1H), 9.37 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 21.84, 55.68, 56.17, 102.24, 103.03, 112.35, 113.06, 128.35, 137.53, 149.77, 150.08, 154.13. MS (EI): 218 (M$^+$, 60), 203 (100), 188 (24), 175 (18), 160 (12), 131 (19), 119 (13). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.55; H, 6.47. Found: C, 71.39; H, 6.49.

Table 2, Entry 7. Preparation of 2-Methyl-3-ethyl-6,9-dimethoxynaphthol and 2-Ethyl-3-methyl-6,9-dimethoxynaphthol. The crude product was purified on a silica gel column, eluting with 25% ethyl acetate in hexane. A mixture of the pure naphthols (0.361 g, 75% yield) was obtained. The regioisomers were separated by loading onto a 1000-micron prep LC plate and eluting twice with 25% hexane in benzene. The upper band yielded the major isomer.

Major isomer (2-methyl-3-ethyl-6,9-dimethoxynaphthol): ^{1}H NMR ($CDCl_3$) δ 1.3 (t, 3H, J = 7 Hz, H at C-5), 2.33 (s, 1H, H at C-1), 2.8 (q, 2H, J = 7 Hz, H at C-4), 3.96 (s, 3H), 4.02 (s, 3H), 6.6 (q, 2H, J = 7 Hz), 7.55 (s, 1H), 9.74 (s, 1H, OH). NOE showed enhancement of H at OH, CH_2 of the Et group, and CH_3 of the Et group upon irradiation of H at C_2 Me and enhancement of H at CH_2 of Et and CH_3 of Et upon irradiation of H at C-4. ^{13}C NMR ($CDCl_3$): δ 11.14, 14.87, 27.45, 55.78, 56.52, 102.02 (C-10), 102.70, 111.11, 111.35, 119.24, 126.29, 143.25, 149.75, 150.06, 151.36. MS (EI): 246 (parent, 71.5), 232 (16.1), 231 (100), 216 (20.8), 203 (8.0), 201 (19.8), 123 (8.3), 98 (8.1), 88 (15.3), 71 (8.7). Anal (on mixture of isomers). Calcd for $C_{15}H_{18}O_3$: C, 73.13; H, 7.3. Found: C, 73.21; H, 7.40.

Minor isomer: mp 109–112 °C. ^{1}H NMR ($CDCl_3$): δ 1.2 (t, 3H, J = 7 Hz), 2.48 (s, 3H), 2.84 (q, 2H, J = 7 Hz), 3.95 (s, 3H), 4.00 (s, 3H), 6.6 (q, 2H, J = 3 Hz), 7.54 (s, 1H), 9.67 (s, 1H, OH). NOE showed enhancement of H at C-4 and the Me of the ethyl group upon irradiation of H at the C_3 Me. ^{13}C NMR ($CDCl_3$): 13.57, 19.62, 20.28, 55.78, 56.39, 102.0, 102.16, 102.48, 114.15, 126.03, 126.1, 136.71, 149.88, 151.13. IR ($CHCl_3$): 3500–3300 (OH), 3000–2900, 1610, 1500, and 1450 (Ph), 1420, 1360, 1250, 1100, 1070 cm^{-1}.

Table 2, Entry 8. Preparation of 2-Methyl-3-ethylnaphthol and 2-Ethyl-3-methylnaphthol. The two isomers were separated by loading the mixture onto a 1000-micron prep plate and eluting twice with 10% ethyl acetate in hexane. The ratio of isomers was 1:1 and the yield was 70%.

Isomer A (2-methyl-3-ethylnaphthol): ^{1}H NMR ($CDCl_3$) δ 1.3 (t, 3H, J = 7 Hz), 2.4 (s, 3H), 2.8 (q, 2H, J = 7 Hz), 5.14 (s, 1H, OH), 7.3 (s, 1H), 7.4 (m, 2H), 7.75 (m, 1H), 8.05 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 11.44, 14.81, 27.32, 116.19, 118.56, 118.77, 120.74, 122.90, 124.66, 125.59, 127.30, 132.89, 141.75. NOE showed slight enhancement of H at C-1 and C-2 upon irradiation of H at C-13, enhancement of H at C-5 upon irradiation of H at OH, and slight enhancement of H at OH and C-1 upon irradiation of H at C-5.

Isomer B (2-ethyl-3-methyl naphthol): ^{1}H NMR ($CDCl_3$) δ 1.25 (t, 3H, J = 8 Hz), 2.5 (s, 3H), 2.8 (q, 2H, J = 8 Hz), 5.2 (s, 1H, OH), 7.3 (s, 1H), 7.4 (m, 2H), 7.7 (m, 1H), 8.05 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 13.8, 19.86, 20.33, 105.07, 120.82, 123.09, 124.61, 124.73, 125.67, 125.58, 127.11, 132.89, 148.0. IR (on a mixture of isomers; $CHCl_3$): 3640–3580 (OH), 3100–2850, 1500, 1390, 1250–1190, 1100, 1050, 920, 850–700, 650 cm^{-1}. MS (EI) (on a mixture of isomers): 186 (parent, 100), 172 (13.8), 171 (93.6), 157 (10.8), 144 (16.4), 141 (8.6), 129 (8.0), 128 (24.4), 127 (6.4), 115 (8.9). HRMS (on a mixture of isomers) found: 186.1047. Calcd for $C_{13}H_{14}O$: 186.1045.

Table 5. Preparation of *trans*-1-(2,5-Dimethoxyphenyl)-2-buten-3-one. A mixture of 2,5-dimethoxybenzaldehyde (5.40 g, 32.0 mmol), 6.5 mL of acetone, 3.5 mL of water, and 0.8 mL of 10% aqueous NaOH was stirred at 23 °C for 6.5 h. The reaction mixture was diluted with 3 N HCl and then extracted with benzene (twice). The benzene extracts were washed with water and then concentrated under vaccum to yield 6.76 g (100%) of crude product. ^{1}H NMR ($CDCl_3$): δ 2.39 (s, 3H), 3.79 (s, 3H), 6.71 (d, J = 16,1 Hz), 6.86 (d, J = 9 Hz, 1H), 6.93 (dd, J = 9, 3 Hz, 1H), 7.07 (d, J = 3 Hz, 1H), 7.86 (d, J = 16 Hz, 1H). The crude product was used without futher purification.

Preparation of *trans*-1-(2,5-Dimethoxyphenyl)-2-buten-3-one, Tosylhydrazone. A mixture of *trans*-1-(2,5-dimethoxyphenyl)-2-buten-3-one (6.72 g, 32.5 mmol) and 6.56 g (35.8 mmol) of *p*-toluenesulfonylhydrazine in 100 mL of methanol containing 0.5 mL of glacial acetic acid was heated at reflux for 10 min. After cooling, the yellow solids were collected, washed with methanol, and dried *in vacuo* to yield 9.42 g (78%) of the

tosylhydrazone. IR ($CDCl_3$): 3016, 2943, 2835, 1597, 1497, 1454, 1385, 1342, 1222, 1165, 1045, 972 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.98 (s, 3H), 2.42 (s, 3H), 3.79 (s, 3H), 3.80 (s, 3H), 6.81 (d, J = 16 Hz, 1H), 6.82 (m, 2H), 7.05 (d, J = 2 Hz, 1H), 7.22 (d, J = 16 Hz, 1H), 7.31 (AA'BB', J = 8 Hz, 2H), 7.44 (broad s, 1H), 7.87 (AA'BB', J = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 11.27, 21.61, 55.83, 56.28, 104.93, 111.05, 112.31, 115.75, 125.56, 128.80, 128.50, 128.65, 129.63, 135.41, 144.17, 151.47, 153.71. Mp: 204 °C (MeOH) decomp. MS (EI): 374 (M^+, 3), 343 (27), 219 (100), 218 (74), 204 (58), 203 (29), 190 (19), 189 (63), 175 (19), 156 (17), 92 (19), 91 (35). Anal. Calcd for $C_{19}H_{12}N_2O_4S$: C, 60.94; H, 5.92. Found: C, 60.62; H, 6.16.

Preparation of 1-Methyl-3-(2,5-dimethoxyphenyl)cyclopropene, 30. A mixture of 0.74 g (2.0 mmol) of the tosylhydrazone and 0.24 g (10.0 mmol) of NaH in 180 mL of 9:1 DME:hexane was irradiated with vigorous mixing for 25 min. The mixture was filtered, and the filtrate was concentrated at reduced pressure to leave a yellow oil residue, which was triturated with hexane and filtered. The filtrate was concentrated and chromatographed on silica gel (9:1 hexane:EtOAc) to yield 0.25 g (66%) of the cyclopropene, >95% pure by ^1H NMR. Attempts to vaccum distill the cyclopropene led to extensive polymerization. IR ($CDCl_3$): 2997, 2943, 2909, 2835, 1605, 1585, 1497, 1466, 1277, 1242, 1215, 1177, 1161, 1049 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.20 (s, 3H), 2.91 (d, J = 2 Hz, 1H), 3.78 (s, 3H), 3.86 (s, 3H), 6.40 (d, J = 3 Hz, 1H), 6.59 (broad s, 1H), 6.66 (dd, J = 8, 3 Hz, 1H), 6.83 (d, J = 8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 10.38, 16.08, 55.47, 56.50, 98.61, 109.57, 111.85, 111.94, 116.16, 137.04, 152.79, 153.87. MS (EI): 190 (M^+, 48), 175 (100), 160 (22), 147 (28), 132 (42), 115 (45), 103 (21), 91 (23), 78 (43). HRMS calcd for $C_{12}H_{14}O_2$: 190.0994. Found: 190.1001.

Reaction of 1-Methyl-3-(2,5-dimethoxyphenyl)cyclopropene (30) with $Mo(CO)_6$. A solution of 56 mg (0.30 mmol) of the cyclopropene in 10 mL of dioxane was added via a syringe to a refluxing solution of 56 mg (0.6 mmoL) $Mo(CO)_6$ in dioxane. The reaction mixture was then refluxed for an additional 5 min. Solvent was removed on a Rotorvap, and the residue was stirred in ether for 3–5 h and then filtered through a pad of Celite. The filtrate was concentrated and purified by column chromatography (silica gel, 4:1 hexane:EtOAc) to yield 41 mg (63%) of the corresponding naphthol, **31**. IR ($CDCl_3$): 3387, 3017, 2955, 2939, 1639, 1616, 1516, 1431, 1389, 1277, 1250, 1215, 1092, 1057 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.44 (s, 3H), 3.93 (s, 3H), 4.00 (s, 3H), 6.05 (m, 2H), 6.77 (s, 1H), 7.49 (s, 1H), 9.37 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 21.84, 55.68, 56.17, 102.24, 103.03, 112.35, 113.06, 128.35, 137.53, 149.77, 150.08, 154.13. Mp: 118–121 °C (hexane). MS (EI): 218 (M^+, 60), 203 (100), 188 (24), 175 (18), 160 (12), 131 (19), 119 (13). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.55; H, 6.47. Found: C, 71.39; H, 6.49.

Preparation of *trans*-1-(1,4-Dimethoxy-2-naphthyl)-2-buten-3-one (33a) and *trans*-1-(1,4,5-Trimethoxy-2-naphthyl)-2-buten-3-one (33b). A solution of 2-bromo-1,4-dimethoxynaphthalene or 2-bromo-1,4,5-trimethoxynaphthalene (0.5 M) in acetonitrile, 5 molar equiv of methyl vinyl ketone, 5 molar equiv of triethylamine, and 0.2 molar equiv of tetrakis(triphenylphosphine)palladium(0) were placed in a sealed Pyrex glass tube and heated at 110–120 °C for 24 h. The volatile components were then removed under vacuum, and the residue was chromatographed on silica gel (4:1 hexane:EtOAc) to yield 73–100% of the enones.

33a: ^1H NMR ($CDCl_3$) δ 2.47 (s, 3H), 3.95 (s, 3H), 4.01 (s, 3H), 6.76 (d, J = 16 Hz, 1H), 6.87 (s, 1H), 7.56 (m, 2H), 8.04 (d, J = 16 Hz, 1H), 8.10 (dd, J = 7, 2 Hz, 1H), 8.23 (dd, J = 7, 2 Hz, 1H).

33b: ^1H NMR ($CDCl_3$) δ 2.46 (s, 3H), 3.92 (s, 3H), 3.98 (s, 6H), 6.76 (d, J = 16 Hz, 1H), 6.90 (s, 1H), 6.95 (d, J = 8 Hz, 1H), 7.46 (dd, J = 8, 8 Hz, 1H), 7.74 (d, J = 8 Hz, 1H), 8.01 (d, J = 16 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 27.17, 56.54, 56.68, 63.44, 101.91, 108.45, 115.50, 119.69, 123.14, 127.48, 128.09, 131.47, 137.70, 150.56, 153.88, 157.48, 198.74. IR ($CDCl_3$): 3001, 2954, 2935, 2843, 1713, 1674, 1651, 1616, 1593, 1381, 1261, 1250, 1126, 1076 cm^{-1}. MS (EI): 287 (9%), 286 (M^+, 49), 256 (20), 255 (100), 229 (17), 214 (54).

Preparation of *trans*-1-(1,4-Dimethoxy-2-naphthyl)-2-buten-3-one, Tosylhydrazone (34a), and *trans*-1-(1,4,5-Trimethoxy-2-naphthyl)-2-buten-3-one, Tosylhydrazone (34b). A 0.04–0.07 M solution of the enone in methanol containing a drop of glacial acetic acid and 2–3 molar equiv of the tosylhydrazine was heated at reflux for 30 min. The reaction mixture was cooled to room temperature, and the yellow solid was collected and washed with methanol, or the crude reaction mixture was chromatographed on silica gel (1:1 hexane:EtOAC) to afford the desired product in 42–84% yield.

33a: mp 199 °C (MeOH) decomp. IR ($CDCl_3$): 3063, 2955, 2932, 2870, 2856, 1593, 1458, 1373, 1339, 1223, 1165, 1092, 1064, 914 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.06 (s, 3H), 2.42 (s, 3H), 3.87 (s, 3H), 4.02 (s, 3H), 6.90 (s, 1H), 6.93 (d, J = 16 Hz, 1H), 7.34 (AA'BB', J = 8 Hz, 2H), 7.40 (d, J = 16 Hz, 1H), 7.53 (m, 2H), 7.90 (AA'BB', J = 8 Hz, 2H), 8.04 (dd, J = 7, 1 Hz, 1H), 8.20 (dd, J = 7, 1 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 11.40, 21.61, 55.79, 63.01, 99.65, 122.24, 122.50, 124.09, 126.20, 127.02, 127.17, 127.92, 128.34, 128.60, 128.65, 129.71, 135.52, 144.22, 148.44, 152.13, 153.59. MS (EI): 424 (M+, 3), 269 (20), 268 (80), 254 (27), 253 (100), 239 (19), 225 (29), 210 (10), 182 (8), 156 (21), 139 (13), 92 (20), 91 (33). Anal. Calcd for $C_{23}H_{24}N_2O_4S$: C, 65.07; H, 5.70. Found: C, 64.94; H, 5.80.

34b: mp 215 °C (MeOH) decomp. IR ($CDCl_3$): 3014, 2935, 2839, 1593, 1454, 1381, 1261, 1165, 1076, 922, 899 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.06 (s, 3H), 2.42 (s, 3H), 3.84 (s, 3H), 3.97 (s, 3H), 3.99 (s, 3H), 6.90 (dd, J = 8, 8 Hz, 1H), 6.92 (s, 1H), 6.93 (d, J = 16 Hz, 1H), 7.33 (s, 1H), 7.34 (d, J = 8 Hz, 2H), 7.40 (d, J = 8 Hz, 1H), 7.42 (d, J = 16 Hz, 1H), 7.68 (d, J = 8 Hz, 1H), 7.90 (d, J = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 11.35, 21.62, 56.52, 56.83, 62.77, 101.96, 107.60, 115.13, 118.86, 124.60, 127.21, 127.94, 128.03, 129.08, 129.71, 131.46, 135.46, 144.24, 148.33, 153.41, 153.76, 157.43. MS (EI): 454 (M^+, 3), 423 (6), 299 (16), 298 (68), 284 (24), 283 (100), 255 (18), 156 (13), 92 (12), 91 (23). Anal. Calcd for $C_{24}H_{26}N_2O_5S$: C, 63.42; H, 5.76. Found: C, 62.96; H, 6.00.

Preparation of 3-(1,4-Dimethoxy-2-naphthyl)cyclopropene (35a) and 1-Methyl-3-(1,4,5-trimethoxy-2-naphthyl)cyclopropene (35b). To a 0.024–0.028 M solution of the tosylhydrazone in dimethoxyethane was added a large excess of NaH in an equal volume of solvent. The mixture was then irradiated as usual for 20–30 min with vigorous stirring. The reaction mixture was diluted with hexane and filtered. The filtrate was concentrated at reduced pressure, and the residue was purified by column chromatography (silica gel, 4:1 hexane:EtOAc, R_f = 0.70 and 0.42, respectively) to give the corresponding cyclopropene in 44–53% yield.

35a: IR ($CDCl_3$) 2943, 2936, 2835, 1624, 1593, 1458, 1370, 1265, 1161, 1119, 1092, 1003, 980 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.20 (d, J = 1 Hz, 3H), 3.05 (d, J = 1 Hz, 1H), 3.91 (s, 3H), 3.94 (s, 3H), 6.26 (s, 1H), 6.67 (m, 1H), 7.39 (ddd, J = 7, 7, 1 Hz 1H), 7.50 (ddd, J = 7, 7, 1 Hz, 1H), 8.04 (d, J = 7 Hz, 1H), 8.16 (d, J = 7 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 10.75, 17.65, 55.46, 62.04, 98.62, 101.19, 116.78, 121.13, 122.11, 124.26, 126.61, 126.40, 128.73, 133.86, 147.67, 151.76. MS (EI) 241 (5), 240 (M^+), 226 (16), 225 (100), 210 (38), 209 (22), 194 (23), 182 (13), 181 (14), 165 (17), 152 (12). HRMS calcd for $C_{16}H_{16}O_2$: 240.1150. Found: 240.1154.

35b: IR ($CDCl_3$) 2955, 2932, 2843, 1597, 1582, 1454, 1381, 1323, 1261, 1126, 1076, 1049, 918 cm^{-1}. ^1H NMR($CDCl_3$): δ 2.19 (s, 3H), 3.01 (d, J = 1 Hz, 1H), 3.88 (s, 3H), 3.91 (s, 3H), 3.95 (s, 3H), 6.30 (s, 1H), 6.65 (d, J = 1 Hz, 1H), 6.80 (d, J = 8 Hz, 1H), 7.38 (dd, J = 8, 8 Hz, 1H), 7.69 (d, J = 8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 10.70, 17.24, 56.42, 56.82, 61.80, 98.46, 104.15, 105.53, 114.19, 116.46, 116.57, 126.44, 131.57, 134.62, 147.85, 153.27, 157.29. MS (EI): 271 (11), 270 (M^+, 58), 256 (17), 255 (100), 240 (28), 239 (44), 225 (18), 224 (34), 223 (12), 211 (19), 209 (16), 181 (11), 165 (11), 128 (14). HRMS calcd for $C_{17}H_{18}O_3$: 238.0993. Found: 238.0993.

Reaction of 3-(1,4-Dimethoxy-2-naphthyl)cyclopropene or 1-Methyl-3-(1,4,5-trimethoxy-2-naphthyl)cyclopropene with $Mo(CO)_6$ To Give Phenanthrols 36a and 36b. A 0.02–0.025 M solution of the cyclopropene in dioxane was added via syringe at the rate of 3.0–6.0 × 10^{-3} mmol/min to a solution of $Mo(CO)_6$ (3 molar equiv, 0.036–0.05 M) in dioxane at reflux. The solvent was removed at reduced pressure, and the residue was diluted with ether and filtered through a pad of Celite. The filtrate was concentrated at reduced pressure, and the residue was purified by chromatography (silica gel, 4:1 hexane:EtOAC) to afford phenanthrol in 20–29% yield.

36a: IR($CDCl_3$) 3583, 3074, 2982, 2835, 1728, 1628, 1454, 1427, 1373, 1350, 1242, 1207, 1146, 1045, 914, 899, 868 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.45 (s, 3H), 4.07 (s, 3H), 5.56 (broad s, 1H), 6.65 (s, 1H), 6.89 (s, 1H), 7.19 (s, 1H), 7.57 (ddd, J = 8, 8, 1 Hz, 1H), 7.65 (ddd, J = 8, 8, 1 Hz, 1H), 8.35 (dd, J = 8, 1 Hz,1H), 9.55 (dd, J = 8, 1 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 21.12, 55.37, 101.98, 104.90, 112.71, 120.40, 121.68, 125.30, 126.43, 126.97, 127.96, 131.34, 135.74, 136.65, 153.82, 153.98. MS (EI): 238 (M^+, 9.1), 195 (28), 184 (19), 165 (34), 152 (23), 119 (68), 109 (25), 105 (30), 97 (19), 89 (25), 88 (40), 83 (20), 82 (31), 76 (28), 69 (100). HRMS calcd for $C_{16}H_{14}O_2$: 238.0993. Found: 238.0994.

36b: IR ($CDCl_3$) 3583, 3035, 2936, 2916, 2835, 1624, 1597, 1574, 1466, 1381, 1354, 1335, 1277, 1250, 1211, 1180, 1134, 1111, 1060, 1015, 972 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.44 (s, 3H), 3.99 (s, 3H), 4.03 (s, 3H), 5.57 (broad s, 1H), 6.64 (d J = 1 Hz, 1H), 6.91 (s, 1H), 7.09 (d, J = 8 Hz, 1H), 7.14 (d, J = 1 Hz, 1H), 7.54 (dd, J = 8, 8 Hz, 1H), 7.27 (d,

J = 8 Hz, 1H). ^{13}C NMR($CDCl_3$): δ 21.06, 56.09, 57.12, 103.93, 109.23, 112.94, 113.50, 117.48, 119.82, 121.18, 127.02, 134.38, 135.79, 136.98, 153.80, 155.50, 157.08. MS (EI): 269 (20%), 268 (M^+, 100), 255 (31), 253 (12), 223 (25), 195 (24), 165 (13), 152 (14). HRMS calcd for $C_{17}H_{16}O_3$: 268.1099. Found: 268.1093.

Preparation of Methyl 3-(1″-Methoxynaphtho[6″,7″-*h*]-2′-keto-6′-(methoxybenzo)pyranyl)propanoate (55). To naphthylchromium carbene complex **53** (1.97 g, 5.20 mmol) in 25 mL of *tert*-butyl methyl ether at 50 °C was added alkyne **54** (1.01 g, 5.49 mmol) in drops over 5 min. After being stirred at 50 °C for 16 h, the mixture was cooled to −40 °C, precipitating a black solid. The solvent was removed with a cannula, and the remaining black solid was dissolved in 10 mL of CH_2Cl_2, cooled to −50 °C, and precipitated by adding 75 mL of pentane. The solvent was removed with a cannula, and the remaining black solid was dried under vacuum for 1 h. The mother liquors from these precipitations were set aside. The black solid and 150 mL of Et_2O were combined in a Parr bomb, pressured with CO to 1200 psi, and heated at 70 °C for 84 h. After filtration through a 3-in. pad of silica gel, the filtrate was evaporated to leave an orange solid. Flash chromatography on silica gel, eluting with hexanes/CH_2Cl_2/Et_2O (10:1:1 to 2:1:1), gave 34 mg (0.08 mmol, 2% recovery) of the pentacarbonyl analog of **53** as an orange solid (R_f = 0.57, 4:1:1 hexanes:CH_2Cl_2:Et_2O) and 216 mg (0.57 mmol, 11% yield) of **55** as a pale orange solid (R_f 0.10, 4:1:1 hexanes:CH_2Cl_2:Et_2O) as well as 5–10-mg quantities of several other compounds which were not characterized. The mother liquors were stirred in air for 1 h and evaporated to leave a red oil. Flash chromatography on silica gel, eluting with hexanes/CH_2Cl_2/Et_2O (20:1:1 to 1:1:1), gave 368 mg (0.97 mmol, 19% recovery) of tetracarbonyl carbene complex **53** and 187 mg (0.49 mmol, 9% yield) of **55** as well as 5–10-mg quantities of several other compounds which were not characterized.

Characterization of 55: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.64 (dd, J = 8.2 Hz, 1H), 3.13 (m, 3H), 3.75 (m, 1H), 3.75 (s, 3H), 4.00 (s, 3H), 4.09 (s, 3H), 6.71 (s, 1H), 7.41 (s, 1H), 7.59 (t, J = 7.3 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 8.36 (d, J = 8.1 Hz, 1H), 9.57 (d, J = 8.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.5, 34.3, 35.8, 52.0, 55.4, 55.8, 95.4, 105.3, 116.4, 117.4, 121.8, 124.5, 126.5, 127.2, 127.4, 128.5, 129.6, 143.0, 150.7, 153.7, 170.1, 171.7. IR (NaCl film, cm^{-1}): 3000 (w), 2952 (w), 2841 (w), 1758 (s), 1737 (s), 1626 (m), 1423 (m), 1308 (m), 1249 (m), 1210 (m), 1160 (s), 1140 (s), 1120 (s). MS (EI): 380 (M^+, 5), 255 (20), 213 (25), 170 (100), 152 (25), 141 (85), 86 (30), 77 (100). HRMS (EI) calcd for $C_{22}H_{20}O_6$: 380.1260. Found 380.1227. Anal. Calcd for $C_{22}H_{20}O_6$: C, 69.47; H, 5.30. Found: C, 69.01, H, 5.46.

Methyl 3-Carbomethoxy-4-(1′-hydroxy-4′9′-dimethoxy-2′-phenanthryl)-butanoate (56a). Sodium (30 mg, 1.31 mmol) was stirred in 10 mL of CH_3OH at 23 °C until it dissolved. Lactone **55** (50 mg, 0.13 mmol) was added, and the mixture was stirred at 23 °C for 2.5 h and then poured into 25 mL of a saturated aqueous NH_4Cl solution. Extraction with 2 × 40 of mL Et_2O, washing with 1 × 50 mL of H_2O and 1 × 50 mL of brine, drying over $MgSO_4$, filtration, and evaporation gave an orange oil. Flash chromatography on silica gel, eluting with hexanes/CH_2Cl_2/Et_2O (2:1:1 to 1:1:1), gave 43 mg (0.10 mmol, 80% yield) of **56a** as an orange waxy solid (R_f = 0.49, 1:1:1 hexanes:CH_2Cl_2:Et_2O). ^{1}H NMR(500 MHz, $CDCl_3$): δ 2.68 (dd, J = 8.0 Hz, 1H), 2.78 (dd, J = 3.4 Hz, 1H), 3.02 (q, J = 10.2 Hz, 1 H), 3.22 (m, 2H), 3.65 (s, 3H), 3.75 (s, 3H), 3.95 (s, 3H), 4.07 (s, 3H), 6.72 (s, 1H), 7.38 (s, 1H), 7.55(t, J = 7.3 Hz, 1H), 7.60(t, J = 7.0 Hz, 1H), 7.79 (s, 1 H – exchanges with D_2O), 8.32 (d, J = 8.2 Hz, 1H), 9.87 (d, J = 8.6 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.8, 35.8, 43.0, 52.3, 52.6, 55.4, 56.1, 95.6, 108.9, 117.6, 118.9, 121.5, 124.7, 125.7, 126.7, 126.9, 131.7, 146.9, 148.1, 153.3, 173.1, 176.1. IR (NaCl film, cm^{-1}) 3660 (w), 2953 (m), 1737 (s), 1713 (s), 1628 (m), 1526 (m), 1426 (m), 1309 (s), 1214 (s), 1161 (s), 1113 (s), 1030 (m), 850(w), 772(w). MS (EI) 396 (M - 16, 5), 380 (M – CH_3OH, 30), 333 (10), 267 (10), 213 (15), 170 (50), 141 (40), 115 (30), 91 (100). Anal. Calcd for $C_{23}H_{24}O_7$: C, 66.98; H, 5.87. Found: C, 66.51; H, 6.00.

Conversion of Methyl 3-Carbomethoxy-4(1′-hydroxy-4′9′-dimethoxy-2′-phenanthryl)butanoate (56a) to Methyl 3(1″-Methoxynaphtho[6″,7″-*h*]-2′-keto-6′-methoxybenzopyranyl)propanoate (55). Phenol **56a** (85 mg, 0.21 mmol), 5 g of silica gel, and 20 mL CH_2Cl_2 were mixed at 23 °C, evaporated to an off-white powder, and dried at 23 °C under high vacuum (0.01 mm) for 9 h. This powder was placed on top of a short silica gel column and eluted with 4:1:1 to 2:1:1 hexanes:CH_2Cl_2:Et_2O to give 68 mg of an orange solid (R_f = 0.25, 2:1:1 hexanes:CH_2Cl_2:Et_2O). Integration of the doublets at δ 9.87 and α 9.57 in the 500-MHz ^{1}H NMR shows a 12% recovery of phenol **56a** and a 74% yield of lactone **55**. This mixture was completely converted to pure lactone by stirring with 5 mg (0.03 mmol) of *p*-TsOH·H_2O in 5 mL of benzene at 23 °C for 10 h. Evaporation of solvent gave 60 mg (0.16 mmol, 77% yield) of lactone **55**.

Improved Procedure for the Synthesis of Methyl 3-Carbomethoxy-4-(1′-hydroxy-4′9′-dimethoxy-2′-phenanthryl)butanoate (56a). Naphthylchromium carbene complex **53** (200 mg, 0.53 mmol), alkyne **54** (107 mg, 0.58 mmol), and 2.7 mL of *tert*-butyl methyl ether were placed in a single-necked flask equipped with a threaded high-vacuum stopcock. The mixture was deoxygenated by the freeze–pump–thaw method (−196 °C/25 °C, three cycles) and back-filled with argon, and the stopcock was sealed at 25 °C. The reaction flask was heated at 50 °C for 16 h. The solvent was then removed at reduced pressure, 15 mL of CH_3OH and 250 mg (4.63 mmol) of $NaOCH_3$ were added, and the resulting slurry was stirred at 23 °C for 2 h. After the reaction was quenched with 50 mL of H_2O, extraction with 2 × 50 mL of Et_2O, drying over $MgSO_4$, filtration, and evaporation gave a red solid. Flash chromatography on silica gel, eluting with hexanes/CH_2Cl_2/Et_2O (10:1:1 to 2:1:1), gave 11 mg (0.03 mmol, 6% recovery) of carbene complex **53** (R_f = 0.54, 4:1:1 hexanes:CH_2Cl_2), a dark red solid, and 58 mg (0.14 mmol, 27% yield) of phenol **56a** (R_f = 0.10, 4:1:1 hexanes:CH_2Cl_2:Et_2O), an orange waxy solid.

Isolation of Methyl 3-Carbomethoxy-4-(1′-hydroxy-4′9′-dimethoxy-2′-phenanthryl)butanoate (56a) as the Acetate, 56b. After the standard reaction of carbene complex **53** with alkyne **54** on a 1.0 mmol scale, the solvent was removed *in vacuo* and triphenylphosphine (1.97 g, 7.5 mmol) was added followed by acetone (20 mL), acetic anhydride (3.24 g, 3.18 mmol), and triethylamine (0.97 g, 9.5 mmol). The volatiles were removed *in vacuo*, and the residue was taken up in ethyl acetate and filtered through Celite. The filtrate was concentrated on the rotary evaporator, and the residue was purified by chromatography on silica gel (hexane/EtOAc). The major product was a tan solid, **56b**, 0.132 g, 44% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.10(dd, J = 0.92, 9.0 Hz, 1H), 8.36 (dd, J = 1.4, 8.0 Hz, 1H), 7.8–7.6 (m, 2H), 7.49 (s, 1H), 7.06 (s, 1H), 4.08 (s, 3H), 4.05 (s, 3H), 3.70 (s, 1H), 3.60 (s, 3H), 3.57 (s, 3H), 3.4–2.5 (m, 4H), 2.53 (s, 3H). ^{13}C NMR (75.47 MHz): δ 174.3, 171.9, 169.3, 153.2, 152.4, 140.4, 130.1, 127.4, 126.6, 126.1, 124.5, 122.4, 120.5, 108.8, 105.1, 100.93, 95.8, 55.7, 55.1, 51.5, 42.2, 42.0, 34.8, 33.7, 20.8. MS (EI): 454 (M^+, 26), 412 (100), 380 (71), 318 (23), 267 (74), 224 (16). HRMS calcd for $C_{25}H_{26}O_8$: 454.1628. Found: 454.1642.

Preparation of Methyl 4-(1′-Hydroxy-4′9′-dimethoxy-2′-phenanthryl)-butanoate, 67a. A solution of complex **66a** (299 mg, 0.755 mmol) in dry MeOtBu (4.0 mL) under argon was heated at 45 °C, and methyl 5-hexynoate (**65**, 116 mg, 119 μL, 0.986 mmol) was added dropwise rapidly. After the mixture was stirred at this temperature for 30 min, the heating bath temperature was lowered and the mixture was allowed to cool. The volatile material was removed at reduced pressure to leave a brown residue. Solid Ph_3P (600 mg, 2.29 mmol) was added followed by acetone (10 mL); the red-black mixture was allowed to stir at 23 °C for 15 h. The volatiles were removed at reduced pressure, and the residue was triturated with EtOAc and filtered through a pad of Celite. The filtrate was concentrated at reduced pressure and purified by column chromatography (SiO_2, 20 × 2-cm column). With increasing amounts of EtOAc in hexane, the major component was eluted with 20% EtOAc in hexane. It was obtained as an orange-yellow gum, 141 mg, 53% yield based on structure **67a**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.97 (dd, J = 1.8, 7.9 Hz, 1H), 8.33 (dd, J = 2.2, 9.7 Hz), 7.88 (s, 1H, OH), 7.63–7.55 (m, 2H), 7.47 (s, 1H), 6.96 (s, 1H), 4.07 (s, 3H), 3.98 (s, 3H), 3.66 (s, 3H), 2.95–2.90 (t, J = 7.65 Hz, 2H), 2.45 (t, J = 7.1 Hz, 2H), 2.06–1.95 (near pentet, J = 7.6 Hz, 2H). ^{13}C NMR(75.47 MHz, $CDCl_3$): δ 174.3, 152.7, 148.3, 146.6, 132.0, 129.1, 127.0, 126.4, 125.6, 124.0, 122.9, 121.6, 117.6, 109.2, 95.9, 55.6, 54.9, 51.1, 32.8, 30.1, 25.5. IR ($CHCl_3$): 2993 (w), 2945 (mw), 2828 (w), 1708 (s), 1625 (ms), 1600 (m), 1570 (w), 1521 (w), 1440 (m), 1425 (ms), 1307 (s), 1265 (s) cm^{-1}. HRMS: 354.1477; calcd for $C_{21}H_{22}O$ 354.1467.

Preparation of Methyl 4-(1′-Hydroxy-4′9′-diacetoxy-2′-phenanthryl)-butanoate, 67b. To a solution of complex **66b** (119 mg, 0.248 mmol) in dry $(nBu)_2O$ (3.0 mL) under argon was added methyl 5-hexynoate (**65**, 52 mg, 53 μL, 0.372 mmol). After the mixture was heated at 65 °C for 12 h, the heating bath temperature was lowered and the mixture was allowed to cool. The volatile material was removed at reduced pressure to leave a brown residue. Solid Ph_3P (204 mg, 0.778 mmol) was added followed by acetone (5 mL); the orange-brown mixture was allowed to stir at 23 °C for 15 h. The volatiles were removed at reduced pressure, and the residue was triturated with EtOAc and filtered through a pad of Celite. The filtrate was concentrated at reduced pressure and purified by column chromatography (SiO_2, 18 × 2-cm column). With increasing amounts of EtOAc in hexane, the major component was eluted with 20% EtOAc in hexane as an amber-yellow gum, 46 mg (47% yield based on

carbene complex **66b**). It was identified as phenthrol **67b** on the basis of spectral data. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.77 (d, J =8.6, 1H), 7.92 (br s, 1H), 7.64–7.56 (m, 2H), 7.33 (s, 1H), 6.74 (s, 1H), 5.79 (br s, 1H, OH), 3.92 (s, 3H), 3.69 (s, 3H), 2.77 (t, J = 6.5 Hz, 2H), 2.48 (s, 3H), 2.40(t, J = 6.3, 2H), 1.85–1.70 (m, 2H). IR ($CHCl_3$): 2990 (w), 2940 (w), 1757 (m), 1727 (m), 1602 (m), 1426 (w), 1368 (w), 1265 (m), 1233 (m) cm^{-1}. MS (EI): 396 (M, 15), 368 (7), 354 (36), 322 (22), 307 (13), 278 (39), 277 (100).

Preparation of 1-Methyl-3-(1,1,4,4-tetramethoxy-2-naphthaquinonyl)-cyclopropene (68). According to the method of Swenton, in a dual cell electrochemical apparatus filled with 1% KOH in methanol was placed 1-methyl-3-(1,4-dimethoxy-2-naphthyl)cyclopropene, **35a** (0.761 g, 3.2 mmol). The apparatus was immersed in an ice/water bath to maintain a reaction temperature between 0 and 10 °C, and a platinum electrode was inserted. The mixture was electrolyzed with a Princeton Applied Research Model 173 potentiostat/galvanostat operating in galvanostat mode set to 100 mA. After 3.5 h the crude mixture was concentrated to ~10% of its volume on a rotary evaporator (without heating) and then partitioned between water (150 mL) and ethyl acetate (100 mL). The organic layer was separated, and the aqueous layer was extracted with additional ethyl acetate (2 × 75 mL). The ethyl acetate layers were combined, washed with an aqueous saturated sodium chloride solution, dried with sodium sulfate, and concentrated on a rotary evaporator to yield 0.733 g (77%) of the desired product (**68**), which is only minimally stable even at reduced temperatures. IR (thin film): 3063, 2974, 2939, 2901, 2827, 1936, 1720, 1658, 1593, 1454, 1369, 1307, 1253, 979 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.25 (d, J = 1 Hz, 1H), 3.03 (d, J = 1 Hz, 1H), 2.95 (s, 3H), 2.98 (s, 3H), 3.15 (s, 3H), 3.20 (s, 3H), 7.44 (m, 1H), 7.65 (m, 1H), 8.04 (d, J = 8 Hz, 1H), 8.18 (d, J = 8 Hz, 1H).

Preparation of 1,4-Diacetoxy-2-naphthaldehyde (71). In a 250-mL round-bottom flask were placed 2-(dibromomethyl)-1,4-diacetoxynaphthalene (4.500 g, 10.82 mmol) and THF (20 mL). The solution was cooled to 0 °C, and silver nitrate (5.520 g, 32.45 mmol) dissolved in water (5 mL) was added dropwise over 5 min. The mixture was stirred for 30 min and then filtered through Celite to remove a gray precipitate. THF (~1/2 the volume) was removed with a rotary evaporator, and the material was partitioned between water (100 mL) and ethyl acetate (200 mL). The aqueous layer was extracted with ethyl acetate (2 × 100 mL). The ethyl acetate layers were combined, washed with a saturated sodium chloride solution, dried with magnesium sulfate, filtered, and concentrated. The crude material was recrystallized from ethyl acetate/hexane (1:2) to yield 2.564 g (87%) of **71** as pale yellow plates, mp 140–142 °C (ethyl acetate/hexane). IR (KBr) 3062, 1762, 1674, 1631, 1604, 1423, 1365, 1199, 1168, 1153, 1064, 1030, 1010, 941, 910, 767, 744 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 2.46 (s, 3H), 2.57 (s, 3H), 7.69 (s, 1H), 7.72 (m, 2H), 8.04 (d, J = 8 Hz, 1H), 8.15 (d, J = 8 Hz, 1H), 10.31 (s, 1H). ^{13}C NMR (acetone-d_6): δ 20.36 (q), 20.61 (q), 115.69 (d), 122.71 (d), 123.83 (d), 125.10 (s), 128.76 (d), 128.90 (s), 130.67 (d), 131.38 (s), 145.78 (s), 148.91 (s), 169.56 (s), 170.13 (s), 188.56 (d). MS: 272 (M$^+$, 2), 231 (5), 230 (32), 189 (25), 188 (100), 187 (15), 186 (9).

Preparation of *trans*-1-(1,4-Diacetoxy-2-naphthyl)-2-buten-3-one (72). In a 250-mL three-neck round-bottom flask was placed sodium hydride (0.154 g, 3.38 mmol, 60% in mineral oil), which was then washed with pentane (3 × 2 mL) and suspended in dimethoxyethane (15 mL). In an addition funnel were placed dimethoxyethane (10 mL) and 2-oxopropyl dimethylphosphonate (0.53 mL, 3.86 mmol), and the mixture was added dropwise over 15 min to the rapidly stirred sodium hydride suspension. The mixture turned cloudy white and was stirred an additional 15 min. In dimethoxyethane (20 mL) was dissolved 1,4-diacetoxy-2-naphthaldehyde, **71** (0.500 g, 1.84 mmol), and this solution was added to the sodium phosphonate mixture dropwise over 20 min. The mixture was stirred an additional 1 h and then poured into water (100 mL), extracted with ethyl acetate (3 × 100 mL), washed with aqueous saturated sodium chloride solution, dried with sodium sulfate, filtered, and concentrated. Chromatography with silica gel eluting with ethyl acetate/hexane (1:1) gave 0.330 g (57%) of a green product, **72**, mp 174–176 °C (acetone). IR (KBr): 3070, 1762, 1674, 1624, 1600, 1419, 1365, 1253, 1188, 1153, 1064, 979, 918, 763, 740 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.39 (s, 3H) 2.49 (s, 3H), 2.56 (s, 3H), 6.78 (d, J = 16 Hz, 1H), 7.51 (s, 1H), 7.59 (m, 2H), 7.68 (d, J = 16 Hz), 7.84 (dd, J = 7, 1 Hz, 1H), 7.86 (dd, J = 7, 1 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 20.50 (q), 20.97 (q), 25.87 (q), 118.50 (d), 121.67 (d), 121.88 (d), 125.24 (s), 127.56 (d), 127.85 (d), 133.47 (d), 140.57 (d), 142.22 (s), 144.12 (s), 168.54 (s), 169.06 (s), 199.57 (s). MS: 312 (M$^+$, 7), 271 (7), 270 (37), 253 (9), 229 (12), 228 (80), 213 (21), 211 (17), 187 (15), 186 (100), 185 (10).

Preparation of *trans*-1-(1,4-Diacetoxy-2-naphthyl)-2-buten-3-one Tosylhydrazone. In a 250-mL round-bottom flask were placed *trans*-1-(1,4-diacetoxy-2-naphthyl)-2-buten-3-one (1.000 g, 3.20 mmol), tosylhydrazide (0.650 g, 3.52 mmol), methanol (50 mL), and 10 drops of glacial acetic acid. The mixture immediately turned bright yellow. The reaction was stirred for 24 h, and a bright yellow precipitate formed. The yellow material was collected by suction filtration and gave 1.215 g (79%) of the desired compound, mp 204 °C (decomp). IR(KBr): 3198, 1762, 1396, 1354, 1207, 1188, 1165, 1064, 1081, 910, 767, 686 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.95 (s, 3H, at C-12), 2.40 (s, 3H, at C-16), 2.43 (s, 3H, at C-14), 2.48 (s, 3H), 6.02 (br s, N*H*), 6.82 (d, J = 16.1 Hz, 1H), 6.94 (d, J = 16.1 Hz, 1H), 7.34 (d, J = 7.2 Hz, 2H), 7.52 (m, 2H), 7.80 (s, 1H), 7.82 (m, 2H), 7.84 (d, J = 7.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 14.59 (q), 20.47 (q), 20.94 (q), 21.56 (q), 119.33 (d), 121.60 (d), 121.72 (d), 125.77 (d), 126.45 (s), 126.99 (d), 127.02 (d), 127.35 (d), 127.92 (s), 128.26 (d), 129.50 (d), 135.37 (s), 139.50 (s), 141.92 (s), 143.97 (s), 144.17 (s), 153.69 (s), 168.54 (s), 169.07 (s).

Preparation of 1-Methyl-3-(1,4-diacetoxy-2-naphthyl)cyclopropene (73). Sodium hydride (0.062 g, 1.56 mmol, 60% in mineral oil) was placed in an Ace Glass photolysis apparatus equipped with an external cooling jacket. The sodium hydride was rinsed with pentane (3 × 2 mL) to remove mineral oil. Dimethoxyethane (100 mL) and *trans*-1-(1,4-diacetoxy-2-naphthyl)-2-buten-3-one tosylhydrazone (0.500 g, 1.04 mmol) were added, and the apparatus was fitted with a long needle through which argon was passed to agitate the solution. The yellow mixture was photolyzed for 6 min with a Hanovia 450-W Hg lamp with a Pyrex filter; the color faded and turned cloudy. Unreacted sodium hydride was destroyed by the addition of water (1 mL). After removing most of the DME on a rotory evaporator, the residue was partitioned between water (100 mL) and ethyl acetate (150 mL), and the layers were separated. The aqueous layer was extracted again with ethyl acetate (2 × 100 mL), and the organic layers were combined, washed with a saturated sodium chloride solution, dried with sodium sulfate, filtered, and concentrated on a rotary evaporator. The material was purified on a silica gel column eluting with hexane/ethyl acetate (4:1) to yield 0.162 g (53%) of a red viscous oil, **73**. ^{1}H NMR ($CDCl_3$): δ 2.15 (d, J = 1 Hz, 3H), 2.41 (s, 3H), 2.47 (s, 3H), 2.65 (d, J = 1.7 Hz, 1H), 6.59 (t, J = 1.3 Hz, 1H), 7.49 (m, 2H), 7.74 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 10.70 (d), 17.80 (q), 20.62 (q), 20.99 (q), 98.12 (d), 115.75 (d), 116.64 (s), 116.67 (s), 121.44 (d), 121.57 (d), 125.64 (d), 126.99 (d), 128.04 (s), 134.92 (s),142.19 (s), 144.47 (s), 169.38 (s), 169.42 (s).

Preparation of 3-(1,4-Naphthoquinon-2-yl)cyclopropene, 69. In a 250-mL round-bottom flask were placed 1-methyl-3-(1,4-diacetoxy-2-naphthyl)cyclopropene (**73**) (0.245 g, 0.83 mmol) and diethyl ether (30 mL). The solution was cooled to 0 °C, and lithium aluminum hydride (4.68 mL, 4.68 mmol, 1 M solution in diethyl ether) was added dropwise over 5 min. The solution was warmed to 25 °C and stirred 0.5 h. Additional diethyl ether (30 mL) was added, and excess LAH was quenced according to the procedure of Fieser.[39] Water (0.18 mL), 15% NaOH solution (0.18 mL), and water (0.54 mL) were added, stirring the mixture for 5 min after each addition. Magnesium sulfate (~0.5 g) was added, and the mixture was stirred 10 min. The mixture was purified by filtration through a column of silica with the aid of additional diethyl ether to yield 0.169 g (87%) of **69** as a dark red oil. ^{1}H NMR ($CDCl_3$): δ 2.18 (d, J = 1.1 Hz, 3H), 2.84 (d, J = 1.2 Hz, 1H), 6.34 (s, 1H), 6.44 (d, J = 1.0 Hz, 1H), 7.73 (m, 2H), 8.05 (dd, J = 3.3, 5.9 Hz, 1H), 8.13 (dd, J = 3.3, 5.9 Hz, 1H). ^{13}C NMR(acetone-d_6): δ 9.85 (d), 16.10 (q), 96.42 (d), 115.16 (s), 126.21 (d), 126.71 (d), 130.43 (d), 133.01 (s), 133.36 (s), 134.14 (d), 134.43 (d), 157.35 (s), 184.94 (s), 186.20 (s).

Preparation of 1-Hydroxy-3-methyl-5,10-anthraquinone, 75. Molybdenum hexacarbonyl (0.100 g, 0.38 mmol) was placed in a 50-mL round-bottom flask, acetonitrile (4 mL) was added, and the solution was heated for 5 h at reflux. The solution was cooled to 25 °C, and 3-(1,4-naphthoquinon-2-yl)cyclopropene (**69**, 0.0612 g, 0.29 mmol) dissolved in acetonitrile (4 mL) was added in one portion to the $Mo(CO)_3(CH_3CN)_3$ solution. After 15 min the mixture was concentrated and applied to a silica gel column, eluting with hexane/ethyl acetate (9:1), to yield 0.0127 g (18%) of the bright yellow anthraquinone, mp 170–172 °C (acetic acid) [lit.[40] mp 174–175 °C). IR ($CDCl_3$): 3686, 1635, 1600, 1361, 1272, 964, 886, 754, 716 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.48 (s, 3H), 7.12 (s, 1H), 7.65 (s), 7.79 (m, 2H), 8.29 (dd, J = 3.6, 6.6, 1H), 8.31 (dd, J = 3.6, 6.6, 1H), 12.57 (s, 1H, O*H*). ^{13}C NMR ($CDCl_3$): δ 22.27 (q), 120.82 (d), 124.02 (d), 126.29 (d), 126.72 (d), 133.08 (s), 133.25 (s),

(39) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; John Wiley & Sons: New York, 1967; Vol. 1, p 584.

133.43 (s), 134.10 (d), 134.51 (d), 137.22 (s), 148.40 (s), 162.66 (s), 182.70 (s), 187.83 (s). MS (EI): 238 (M^+, 100), 237 (13), 223 (6), 210 (10), 209 (5).

Acknowledgment. The cyclopropene rearrangment study was done at Princeton with support from NIH GM31352. The naphthalene benzannulation studies were done at Princeton (NIH GM31352) and at Chicago (NIH CA32974).

Supplementary Material Available: Complete details regarding the X-ray diffraction analysis comprised of a list of parameters, the ORTEP diagram, and 10 tables (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.