Rhodium(II)-Catalyzed Decomposition of 1-Diazo-4-(1- or 2-naphthyl)-2-butanones as a New Route to Rearranged Pimarane and Abietane Skeleta. Synthesis of Umbrosone

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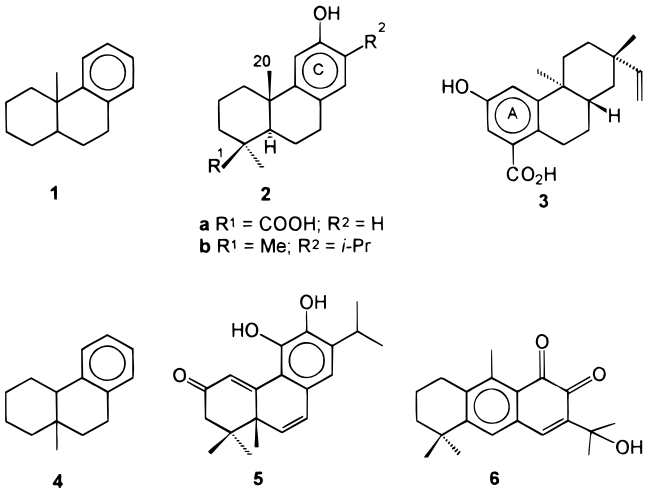
The $Rh_2(OAc)_4$-catalyzed intramolecular Buchner reaction of 1-diazo-4-(1- or 2-naphthyl)butan-2-ones was examined as a potential route to abietane and rearranged abietane derivatives. Treatment of the α-diazo ketone **26** with catalytic amount of dirhodium tetraacetate in CH_2Cl_2 at 0 °C furnished the tetracyclic derivative **27** in good yield. Addition of TFA to **27** (in CH_2Cl_2) resulted in an acid-induced opening of the cyclopropane ring to give the 4a- and 10a-methyldihydrophenanthrenones **28** and **29** in nearly equal amounts. These compounds and their analogs appear to be suitable intermediates for the synthesis of diterpenoids containing aromatic A or C rings. When the diazo ketone **34** was decomposed under Rh(II) catalysis, a 10-methyldihydroanthracenone (*i.e.*, **36**) was obtained as the main product, besides minor amounts of the expected tetracyclic ketone **35**. The extension of this result to the preparation of the methoxy-substituted dihydroanthracenone **39** (52% yield) was exploited in a new total synthesis of umbrosone (**6**), an unusual diterpenoid possessing a rearranged linear skeleton.

The 4a-methyloctahydrophenanthrene system **1** and its 10a-methyl isomer **4** are present in a number of tricyclic diterpenoids with an aromatic C or A ring,[1] such as podocarpic acid (**2a**),[2] ferruginol (**2b**),[3] *ar*-maximic acid (**3**),[4] and pygmaeocin C (**5**).[5] If properly functionalized, **1** and **4** could serve as useful intermediates in the synthesis of policyclic diterpenoids[6] as well as of a wide range of triterpenoids, steroids, and steroidal alkaloids. Although the preparation of the structural unit **1** has been accomplished in a variety of ways,[7−11] none of them involved a stereospecific methyl group migration giving rise to the 4a-center with a predetermined configuration. In the case of the less common system **4**,[12,13] acid-promoted 20(10-5)-*abeo* rearrangements of 8,11,13-abietatriene derivatives have been described.[14]



Recently, we found[15] that the 1,2-dihydrophenanthren-3(4*H*)-one (**9**) can be obtained in almost quantitative yield by TFA treatment of compound **8**, which in turn was easily prepared from **7** through a rhodium(II)-promoted intramolecular Buchner reaction (Scheme 1A).[16] An analogous reaction sequence, when performed starting

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(8) AB → C sequence; *inter alia cf.* (a) Spencer, T. A.; Weaver, T. D.; Villarica, R. M.; Friary, R. J.; Posler, J.; Schwartz, M. A. *J. Org. Chem.* **1968**, *33*, 712. (b) Spencer, T. A.; Friary, R. J.; Schmiegel, W. W.; Simeone, J. S.; Watt, D. S. *J. Org. Chem.* **1968**, *33*, 719.

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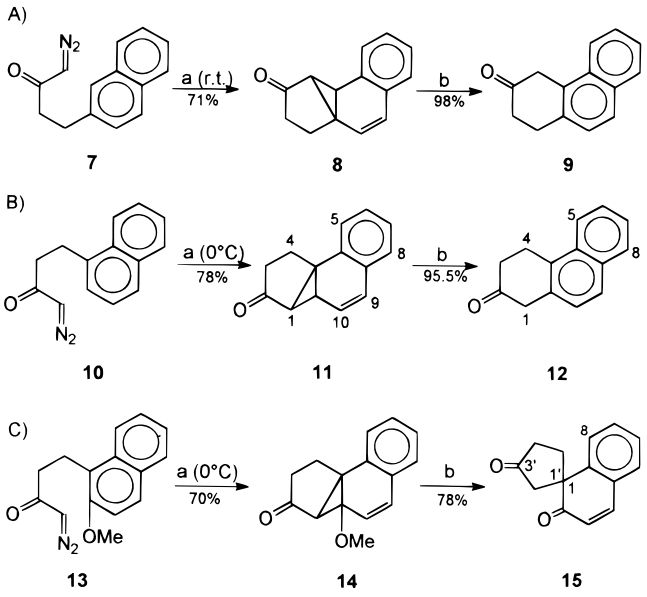
Scheme 1[a,b]

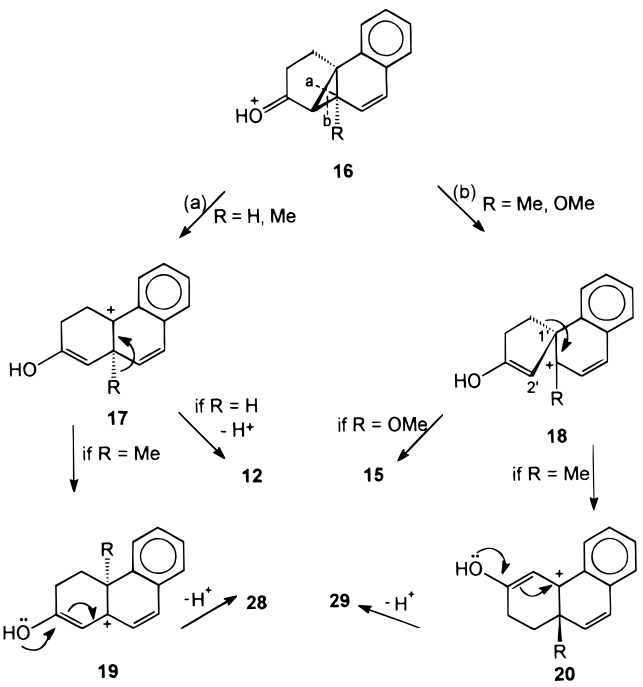


[a] Reaction conditions: (a) $Rh_2(OAc)_4$, CH_2Cl_2; (b) TFA, CH_2Cl_2, rt. [b] Phenanthrene numbering is arbitrarily used for the tetracyclic derivatives to make clear their structural correlation and comparison of their NMR data with those of dihydrophenanthrenones.

from 1-diazo-4-(1-naphthyl)butan-2-one (**10**),[17] gave the tetracyclic ketone **11**, whose structure was proved by comparison of its NMR data with those of **8**[15] (in addition ^{1}H NOEs were observed in **11** between H-1 and H-10 and between H-5 and H-4). The 3,4-dihydrophenanthren-2(*1H*)-one (**12**)[18] was then obtained by treating **11** with TFA (Scheme 1B). The isolated yields of compounds **11** and **12** confirmed the applicability of the intramolecular naphthalene cyclopropanation to synthesize dihydrophenanthrenones with the carbonyl function at 2- or 3-position.

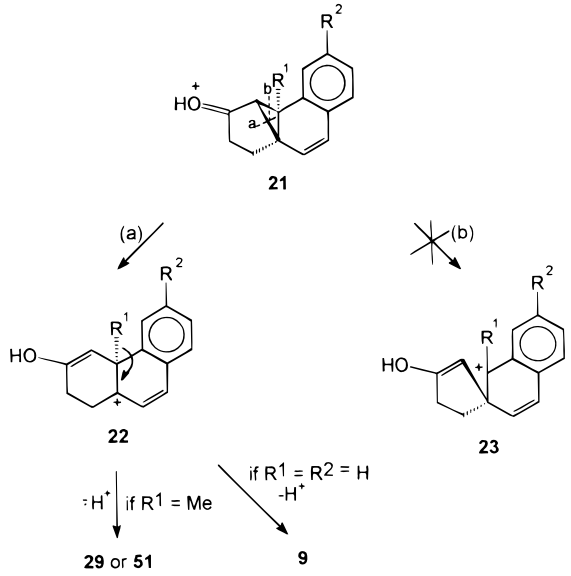
The high selectivity in the formation of **12** and **9** as end products of the cyclopropane ring opening may be understood if one considers the cation stabilization in the pairs **17**/**18** (Scheme 2, R = H) and **22**/**23** (Scheme 3, $R^1 = R^2 = H$), respectively. All of them being in conjugation with the phenyl group, it is likely that the tertiary carbocations are favored with respect to the secondary ones. In addition, the easy rearomatization of ring B by subsequent deprotonation of the angular cation predominates over other possible routes having spiranic cations as intermediates. Lacking aromatization as a driving force, the electronic stabilization of the carbocation must be the main guiding factor in determining the particular cyclopropane bond that breaks under the attack of the electrophile.[10,19] This appears to be consistent with two facts: (i) by the action of dry HCl in $CHCl_3$ on compounds **24a,b** the benzylic cation prevails over the unconjugated

Scheme 2[a,b]



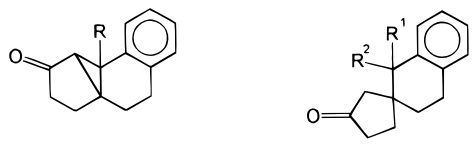
[a] R = H, Me, OMe. [b] For clarity, one enantiomer is depicted.

Scheme 3[a,b]



[a] R^1 = H, Me. R^2 = H, OMe. [b] See note b of Scheme 2.

one, so that the spiro derivatives **25a**,**b** are formed as the only reaction products;[19c] (ii) TFA treatment of the



tetracyclic compound **14** [^{1}H NOE from Me to H-1 (1%); from Me to H-10 (2%)] resulting from the decomposition of the 1-diazo-4-(2-methoxy-1-naphthyl)butan-2-one (**13**)

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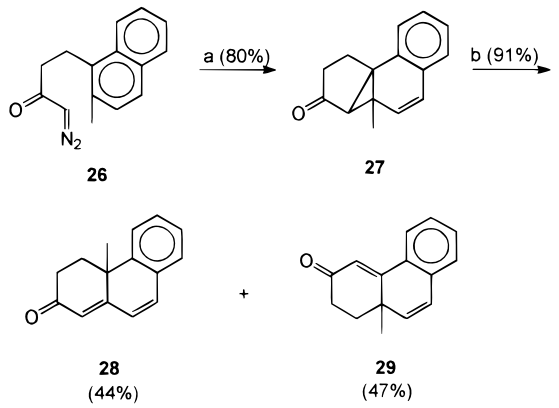
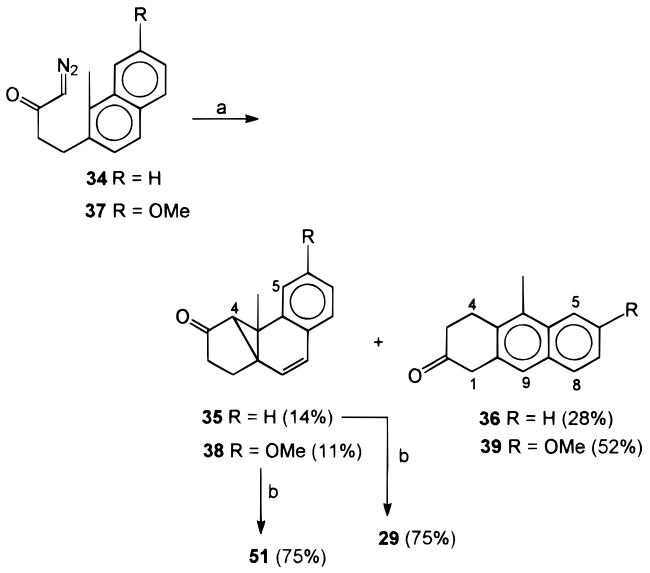
Scheme 4[a]



[a] Reaction conditions: (a) $Rh_2(OAc)_4$, CH_2Cl_2, 0 °C; (b) TFA, CH_2Cl_2, rt.

Scheme 5[a]



[a] Reaction conditions: (a) $Rh_2(OAc)_4$, CH_2Cl_2, 0 °C; (b) TFA.

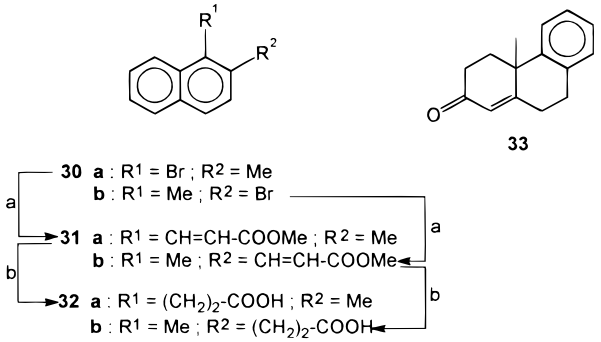
furnished the spiro derivative **15** [IR ($CHCl_3$) 1660, 1743 cm^{-1}; NOE association of H-2′ with H-8 (1.3%)] (Schemes 1C and 2). The latter outcome is clearly due to a strong stabilization of the cation **18** (R = OMe) by the electron donor methoxy group which eventually gives rise to the carbonyl function.

In view of the above findings our attention was directed to the reactions of sequences B and A of Scheme 1 starting from diazo ketones with a methyl group in the *β*- or α-position of the naphthalene nucleus, respectively. The aim was to examine the effects of this substitution both on the regioselectivity in the attack of the electrophilic metal carbene[20] upon the naphthalene nucleus and on the evolution of cations resulting from cyclopropane opening in species such as **16** (R = Me) and **21** (R^1 = Me, R^2 = H or OMe), rearomatization being precluded in any case.

We report here a new route to 4a-methyl-4,4a-dihydrophenanthren-2(3*H*)-one (**28**) and 10a-methyl-1,10a-dihydrophenanthren-3(2*H*)-one (**29**) (Schemes 4 and 5) based on the $Rh_2(OAc)_4$-catalyzed decomposition of methyl-substituted 1-diazo-4-(1- or 2-naphthyl)-2-butanones **26** or **34**, followed by acid treatment of the resulting tetracyclic ketones **27** or **35**. It can be pointed out that an extension of this procedure starting from analogs of the α-diazo ketones **26** or **34** with appropriate substituents would provide convenient entries to the synthesis of podocarpanes (e.g., **2a**), abietanes (e.g., **2b**), and 20(10-9)-*abeo*-pimaranes (e.g., **3**) as well as 20(10-5)-*abeo*-abietanes (e.g., **5**). In addition, the isolation of 10-methyl-3,4-dihydroanthracen-2(1*H*)-ones **36** and **39** as the most abundant reaction products in the Rh(II)-induced decomposition of the diazo ketones **34** and **37** (Scheme 5) suggests a new way to obtain rearranged linear abietanes.[21] This opportunity has been exploited by us to achieve a formal total synthesis of umbrosone (**6**),[21b] an unusual diterpenoid present in the roots of *Hyptis umbrosa* and possessing antimicrobial activity.[21c]

Results and Discussion

$Rh_2(OAc)_4$ Decomposition of 1-Diazo-4-(2-methyl-1-naphthyl)-2-butanone (26). The diazo ketone **26** was obtained from 1-bromo-2-methylnaphthalene (**30a**)[22] *via* the Heck reaction[23a] with methyl acrylate,[23b] followed by hydrogenation of the resulting *(E)*-unsaturated ester (**31a**) and hydrolysis to 3-(2-methyl-1-naphthyl)propionic acid (**32a**).[17] When **26** was treated with catalytic amounts



Reaction conditions: (a) methyl acrylate, Et_3N, $Pd(OAc)_2(PPh_3)_2$, reflux; (b) H2 + Pd/C; KOH/EtOH, reflux.

of dirhodium tetraacetate in CH_2Cl_2 at 0 °C for 3 h, the reaction product (80% isolated yield) was shown to be the expected cyclopropane derivative **27** on the basis of NMR analogies with compound **11** (in particular ^{1}H NOE correlations of Me with H-10). Addition of TFA (a few drops) to a CH_2Cl_2 solution of **27** at rt for 15 min afforded nearly equal amounts of two compounds which were separated by column chromatography. The more polar of these (44% isolated yield) was shown to be the known 4a-methyl-4,4a-dihydrophenanthren-2(3*H*)-one (**28**)[12,24] while the structure 10a-methyl-1,10a-dihydrophenanthren-3(2*H*)-one (**29**) was assigned to the other reaction product (47%) taking account of its spectral data: in particular, the presence of an α,*β*-unsaturated carbonyl

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group was supported by IR ($CHCl_3$ 1653 cm^{-1}) and UV [λ_{max} (log ϵ) (MeOH) 258 (4.38), 306 (3.96), 348 (3.68) nm] spectra, while the position of the methyl group and of the two olefinic bonds was confirmed by ^1H NOE experiments [correlations between H-8 (δ 7.13) with H-9 (δ 6.43), H-4 (δ 6.34) with H-5 (δ 7.68), and Me (δ 1.27) with H-10 (δ 5.86)] (*cf.* ref 5).

The origin of the two isomeric dihydrophenanthrenones **28** and **29** can be rationalized as shown in Scheme 2 (R = Me), *i.e.*, in terms of a tendency of cations **17** and **18**, resulting from the protonation of the cyclopropyl ketone (as in **16**), to collapse to the more stable cations **19** or **20** through the migration of the angular methyl group or of the C(1′)−C(5′) bond, respectively.[25] A ready deprotonation of the initially formed enol group then concludes both rearrangements. Apparently, the presence of the methyl group both precludes the ring B aromatization and stabilizes the spiranic cation **18** that becomes competitive with **17**. In principle, the conversion of **16** into the rearranged carbocations **19** and **20** could occur *via* concerted mechanisms.[10a]

Compound **28**, first prepared by reaction between 1-methyl-2-naphthol and methyl vinyl ketone,[7f] has been shown to be a potential intermediate in the synthesis of resin acids related to podocarpic acid (**2a**)[27] since it can be converted into the key synthon **33** by reduction with lithium in liquid ammonia.[27a] In addition, the presence of the diene system in compound **28** makes it (or its analogs with appropriate substituents in ring C) particularly suitable for synthesizing ring B oxygenated diterpenoids.[1,6] The availability of the 10a-methyl-1,10a-dihydrophenanthren-3(2*H*)-one (**29**) from the route of Scheme 2 (and from that described in Scheme 3, *vide infra*) opens a new access to the system **4**. It can be noticed that the functionality of rings A and B of **29** is the same as in pygmaeocins B and C (**5**).[5,13,14]

Considering the unquestionable stereospecificity in the rearrangements outlined in Scheme 2, chiral compounds such as **28** and **29** could be obtained in a stereochemically defined configuration provided their tetracyclic precursor is produced in enantiomerically pure form. In this regard, efforts are being made in the light of recent advances in the design and development of chiral catalysts for asymmetric reactions of metal carbenes.[28,29]

$Rh_2(OAc)_4$ Decomposition of 1-Diazo-4-(1-methyl-2-naphthyl)-2-butanone 34 and 37. 2-Bromo-1-methylnaphthalene (**30b**)[30] was converted into the α-diazo ketone **34** through the intermediates **31b** and **32b** in the same way used to prepare compound **26**.[17] On treatment of **34** with dirhodium tetraacetate, as previously described, two products were isolated from the reaction mixture by flash chromatography. One of them was found to be the expected tetracyclic ketone **35** by comparison of its NMR spectra with those of compound **8**[15] and by NOE correlations [from Me to H-5 (7.2%); from H-5 to Me (1%)]. The other showed spectroscopic data consistent with the presence of a methyl group linked to an aromatic ring (δ 2.68), of an unconjugated keto group [IR($CHCl_3$) 1715 cm^{-1}], and of a naphthalene system [UV λ_{max} (log ϵ) (MeOH) 232 (5.16), 276 (4.04) nm]. The structure of 10-methyl-3,4-dihydroanthracen-2(1*H*)-one (**36**) was assigned to it on the basis of additional ^1H NOE experiments (7.3% and 2.7% intensity enhancement of H-5 and H-4, respectively, by irradiation of the methyl protons, and 2.6% enhancement of H-9 by irradiation of H-1).

The isolation of compound **36** as the more abundant product (its ratio to **35** was found to be *ca* 2 by NMR analysis of reaction mixture from repeated preparations) deserves some comments. This result appeared to be rather surprising in view of the well-recognized preference for five-membered-ring formation exhibited by intramolecular metal carbene reactions with dirhodium(II) carboxylates as catalysts.[16,31] However, exceptions are known[31c] which can be attributed to steric factors[32] or to electronic stabilization of the developing electrophilic center resulting from a six-membered ring closure.[33] Compound **36** may derive from an insertion reaction of the carbenoid center into the C(3)−H bond of the aromatic nucleus,[34] but the production of compounds of formal aromatic C−H insertion is generally thought to involve an addition−elimination mechanism.[31c,35] The intramolecular electrophilic addition of the rhodium carbene to form a six-membered carbocation intermediate, which undergo ready deprotonation[33] with concurrent dissociation of the catalyst to complete the overall substitution reaction [as depicted in Scheme 6, path b], seems the most likely explanation for the origin of **36**. In fact, it is improbable that a cycloaddition to the 2,3-side of the naphthalene nucleus occurs giving rise to the nonaromatic compound **43** (R = Me) which then undergoes cleavage of the cyclopropane ring under the action of the electrophilic metal catalyst.[20] A rapid rearomatization of **43** (R = Me) would take place *via* cycloreversion with formation of the dihydrobenzoazulenone **44** (R = Me). Such a norcaradiene−cycloheptatriene isomerization[36] does occur from **43** (R = H) to **44** (R = H) in the $Rh_2(OAc)_4$-induced decomposition of **7**, whose reaction mixture was found to contain the compound **45** (8% isolated yield) as the only stabilization product of **43** (R = H).[15]

(25) Carbocations at the 6-position of 1-methylbicyclo[4.4.0]decane systems are known to rearrange in different manners according to their origin and structure: with methyl migration [(I)-Type][14,26b,d], with a cyclohexane bond migration forming a spiranic cation [(II)-Type][26a], with cyclohexane ring cleavage [(III)-Type].[14,26b−e]

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(29) It can be noted that enantiomerically enriched 4a-methyl-4,4a,9,10-tetrahydrophenanthren-2(3*H*)-ones, e.g., **33**, have so far been prepared by enantioselective Michael addition reactions using a chiral enamine as donor (80−93% ee)[7c,e,9a] or a chiral phase transfer catalyst,[7d] and *via* asymmetric Heck reaction.[9e]

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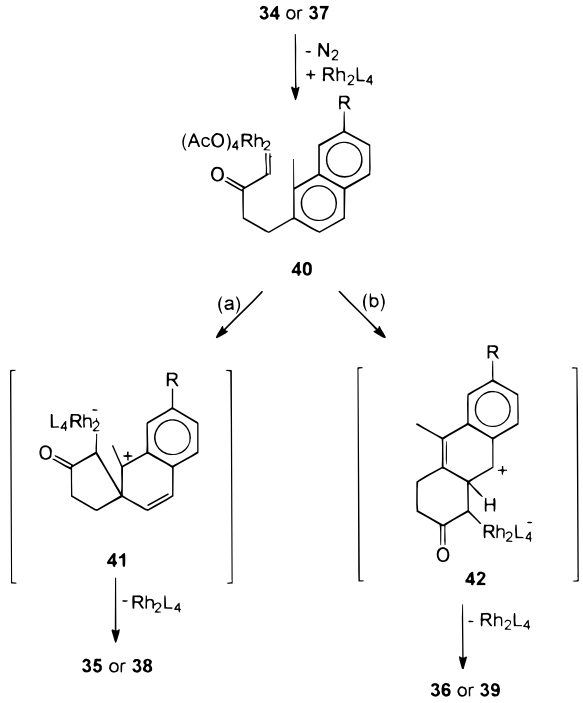
Scheme 6

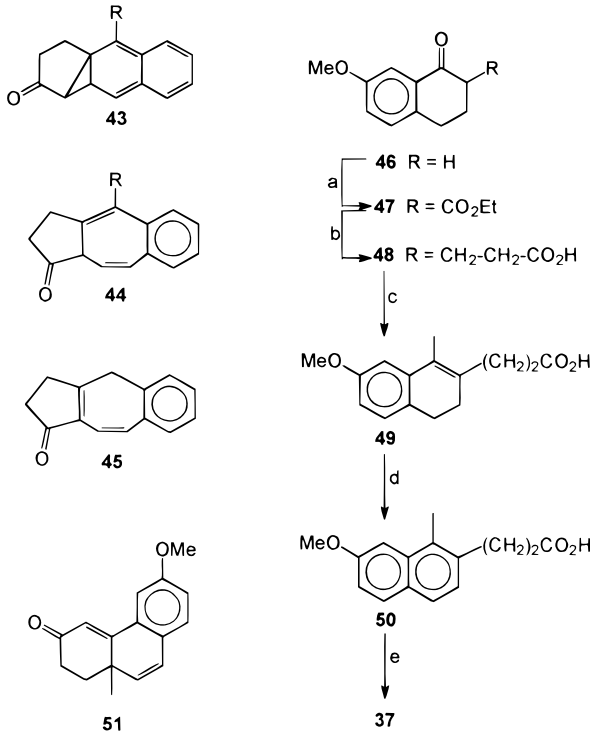


Steric interactions are presumably responsible for the preference of path b over path a in Scheme 6. One can presume that a relevant repulsion develops between the bulky end[37] of the tether and the adjacent methyl group of the metal carbene **40**, either at the π-complex or in the transition state (formally represented by **41**)[20] preceding the formation of the cyclopropane ring.

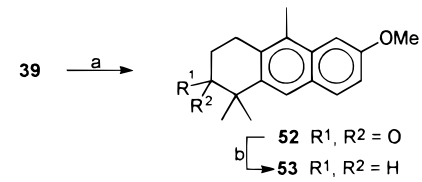
In accordance with the dichotomic mechanism of Scheme 6, a marked increase of the regioselectivity in favor of the dihydroanthracenone derivative **39** was observed in the Rh(II)-catalyzed decomposition of **37** (Scheme 5). This result can be attributed to an extra stabilization of the benzylic cation **42** (Scheme 6) by the *p*-methoxy group. Compound **37** was prepared through the reaction sequence from 7-methoxy-1-tetralone (**46**) to **50** followed by the usual conversion of the arylpropionic acid into the corresponding diazo ketone.[17]

As regards the acid-catalyzed opening of the cyclopropane ring of **35** and **38** (Scheme 5), only compounds resulting from a methyl shift, *i.e.*, **29** and **51**, respectively, were obtained. The complete predominance of path a over path b from **21** (Scheme 3), when compared to the outcome from collapsing **16** (Scheme 2), may be explained in terms of an additional stabilization of the nonspiranic cation **22** by vinylology.

Synthesis of Umbrosone (6). With compound **39** in hand, we were able to transform it into 6-methoxy-1,1,10-trimethyl-1,2,3,4-tetrahydroanthracene (**53**) through dimethylation of C-1 and reduction of the carbonyl group of **52**. Compound **53** had previously been prepared from the Hagemann's ester (10 steps, 11.5% yield)[21c] and from (+)-dehydroabietic acid (16 steps, 0.25% yield).[21d] Since the conversion of **53** into **6** is described,[21c,d] our preparation of the tetrahydroanthracene **53** from 7-methoxy-1-tetralone (**46**) (8 steps, 24.1% yield) represents a new (formal) synthesis of umbrosone (**6**). In addition, it can be pointed out that the presence of a keto group in the 2-position of the 10-methyl-1,2,3,4-tetrahydroanthracene skeleton makes 1-diazo-4-(1-methyl-2-naphthyl)butan-2-ones suitable starting materials for the synthesis of ring-A functionalized linear abietanes (e.g., pygmaeocin E).[21a] These unusual diterpenoids are the subject of great interest, due to their potential bioactivity.[21a−e]



Reaction conditions: (a) NaH, $(EtO)_2CO$ (98%); (b) EtONa, ethyl acrylate; KOH/HCl (95%); (c) MeMgI; H_2SO_4 (88%); (d) DDQ (89%); (e) $(COCl)_2$; CH_2N_2 (75%).



Reaction conditions: (a) *t*-BuOK, MeI (88%); (b) Ts-NH-NH_2/AcOH (98%); $NaCNBH_3$/sulfolane-DMF (85%).

Experimental Section

All melting points are uncorrected. Elemental analyses were obtained in-house. Solvents were purified and dried according to standard literature procedures. Analytical TLC was performed on silica gel F_{254} precoated aluminum sheets (0.2 mm layer, Merck; eluent systems: A, hexane:ethyl acetate 1:1; B, hexane:ethyl acetate 2:1; C, hexane:ethyl acetate 8:1; D, hexane:ethyl acetate:diethyl ether 75:10:15; E, hexane:ethyl acetate 9:1; F, hexane:chloroform 1:3; G, hexane:ethyl acetate 5:1). Visualization was accomplished with UV light or sulfuric acid solution (10% methanol). Silica gel (40−63 μm) from Merck was used for flash chromatography.

Preparation of diazo Ketones. All diazo ketones were prepared from the corresponding 3-naphthylpropionic acids in good yields (70−90% overall yields).[17] The following procedure is representative.

In a round-bottomed two-necked flask, under a nitrogen atmosphere, 4.2 mequiv of acid were mixed with 24 mL of dry

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CH_2Cl_2. The solution was cooled in an ice bath, and oxalyl chloride in 20% excess was added slowly. After the addition was complete the mixture was heated to reflux. The reaction was monitored by IR spectroscopy, following the disappearance of the band at ca. 1700 cm^{-1}. At the end of the reaction, the solvent was removed by rotary evaporation to give the acyl chloride in 90−95% yield, which was used without further purification.

Under magnetic stirring, 1 mequiv of the acyl chloride in 8 mL of dry ether was dropped into 3 mequiv of CH_2N_2 (0.5 M in dry ether) under nitrogen atmosphere, cooling the solution with an ice bath. The reaction mixture was left to stand at room temperature for 2 h, monitoring the reaction progress by TLC (eluent system B). After evaporation of the solvent the crude product was purified by flash chromatography using eluent B to give the diazo ketone pure enough for the next transformation.

1-Diazo-4-(1-naphthyl)-2-butanone (10). A well-stirred mixture of 2-naphthaldehyde (24 g, 154 mmol), malonic acid (32 g, 306 mmol), and piperidine (12 mL) in pyridine (180 mL) was refluxed for 2 h. After cooling, the reaction mixture was poured into concentrated HCl (250 mL) containing crushed ice. The flocculent white precipitate was collected by suction filtration and dried in a vacuum desiccator to give 3-(1-naphthyl)acrylic acid (26.1 g, 86%) as a white solid: mp 212−213 °C (lit.[38] mp 214−215 °C); TLC (eluent A, R_f 0.46); EIMS *m*/*e* (rel intensity) 198 (M^+, 50), 153 (100), 79 (24); ^{1}H NMR (acetone-d_6) δ 8.52 (d, J = 15.0 Hz, 1H), 8.3−7.5 (m, 7H), 6.61 (d, J = 15.0 Hz, 1H). Anal. Calcd for $C_{13}H_{10}O_2$ (198.22): C, 78.70; H, 5.04. Found: C, 78.68; H, 5.11.

The naphthylacrylic acid (13 g, 65.6 mmol) in ethyl acetate (600 mL) was then hydrogenated at 1 atm and 23 °C in the presence of 10% palladium on charcoal (4.3 g). After 4 h the catalyst was filtered off and the filtrate evaporated to provide the crude 3-(1-naphthyl)propionic acid which was recrystallized from acetone (93% yield): mp 157.7−158.7 °C; TLC (eluent A, R_f 0.5); ^{1}H NMR ($CDCl_3$) δ 8.13 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.5 Hz, 1H), 7.78 (m, 1H), 7.57−7.40 (m, 4H), 3.43 (t, J = 7.5 Hz, 2H), 2.77 (t, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 173.44, 137.23, 132.03, 129.00, 127.14, 126.15, 125.79, 123.70, 34.60, 27.98. Anal. Calcd for $C_{13}H_{12}O_2$ (200.22): C, 77.98; H, 6.04. Found: C, 77.76; H, 6.19.

10: yellow solid (90% yield); mp 56.5−57.5 °C; TLC (eluent B, R_f 0.6); IR ($CHCl_3$) 2104, 1634 cm^{-1}; UV: λ_{max} (log ϵ) (MeOH) 228 (4.72), 276 (3.90); ^{1}H NMR ($CDCl_3$) δ 8.02 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.53−7.26 (m, 4H), 5.13 (br s, 1H), 3.43 (t, J = 7.5 Hz, 2H), 2.79 (br t, 2H); ^{13}C NMR ($CDCl_3$) δ 193.81, 136.57, 133.84, 131.48, 128.82, 127.02, 126.02, 125.52, 123.28, 54.50, 41.44, 27.89. Anal. Calcd for $C_{14}H_{12}N_2O$ (224.09): C, 74.97; H, 5.40; N, 12.50. Found: C, 75.03; H, 5.50; N, 12.25.

1-Diazo-4-(2-methoxy-1-naphthyl)-2-butanone (13). (Carbethoxymethyl)-triphenylphosphonium bromide (8.9 g, 23 mmol) in 50 mL of absolute ethanol was added slowly under a nitrogen atmosphere and vigorous magnetic stirring to 30 mL of a solution of sodium (0.58 g, 25.2 mmol) in absolute ethanol. After the precipitation of sodium bromide was complete, 2-methoxy-1-naphthaldheyde (4.3 g, 23 mmol) in 10 mL of absolute ethanol was dropped and the reaction mixture left to stand for 48 h. The disappearance of the aldehyde was monitored by TLC (eluent B, R_f 0.5). KOH (1 g) was then added and the reaction mixture heated to reflux for 30 min. After the solvent was removed under reduced pressure, the residue was dissolved in water and extracted with ether. The aqueous layer was acidified with concentrated HCl and extracted with ether (3 × 50 mL), and the solvent was evaporated to give 3-(2-methoxy-1-naphthyl)acrylic acid (4.7 g) which was recrystallized from ethanol−H_2O 2:1 (90% yield): mp 163.5−165 °C; TLC (eluent A, R_f 0.5); IR ($CHCl_3$) 2972, 1678 cm^{-1}; UV λ_{max} (log ϵ) (MeOH) 234 (3.33), 318 (2.63), 350 (2.62); ^{1}H NMR ($CDCl_3$) δ 8.53 (d, J = 16 Hz, 1H), 8.23 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 9 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.32 (d, J = 9 Hz, 1H), 6.86 (d, J = 16 Hz, 1H), 4.05 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 173.00, 139.86, 132.07, 128.57, 127.56, 123.89, 123.04, 122.00, 112.63, 56.14. Anal. Calcd for $C_{14}H_{12}O_3$ (228.25): C, 73.67; H, 5.30. Found: C, 73.70; H, 5.34.

Naphthylacrylic acid (4.7 g, 21 mmol) in ethyl acetate (250 mL) was hydrogenated at 1 atm and 23 °C in the presence of 10% palladium on charcoal (1 g). After 4 h the catalyst was filtered off and the filtrate evaporated to provide 3-(2-methoxy-1-naphthyl)propionic acid in 95% yield: mp 130−131 °C from ethanol−H_2O 2:1; TLC (eluent A, R_f 0.5); IR ($CHCl_3$) 2937, 1707 cm^{-1}; UV λ_{max} (log ϵ) (MeOH) 230 (4.51), 282 (3.35), 294 (3.29); ^{1}H NMR ($CDCl_3$) δ 7.98 (d, J = 9 Hz, 1H), 7.78 (t, J = 9 Hz, 2H), 7.50 (t, J = 9 Hz, 1H), 7.34 (t, J = 9 Hz, 1H), 7.27 (d, J = 9 Hz, 1H), 3.95 (s, 3H), 3.45 (t, J = 8.4 Hz, 2H), 2.67 (t, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 179.19, 154.45, 132.03, 129.15, 121.23, 128.58, 128.17, 126.66, 123.23, 122.63, 113.03, 56.27, 33.98, 21.00. Anal. Calcd for $C_{14}H_{14}O_3$ (230): C, 73.03; H, 6.13. Found: C, 73.20; H, 6.16.

13: yellow solid (79% yield); mp 61.5−63 °C; TLC (eluent B, R_f 0.6).

1-Diazo-4-(2-methyl-1-naphthyl)-2-butanone (26). Diacetatobis(triphenylphosphine)palladium(II) was prepared by adding an eccess of triphenylphosphine (*ca*. 0.35 g) in 20 mL of benzene to a solution of $Pd(OAc)_2$ (0.2 g) in 20 mL of benzene. Addition of petroleum ether (60−80 °C) to the resulting pale yellow solution gave, on shaking slowly, lemon yellow crystals of the complex, mp 135−136 °C, which were washed with petroleum ether and dried *in vacuo* (40 °C). Methyl acrylate (0.76 g, 8.8 mmol), 1-bromo-2-methylnaphthalene (**30a**) (1.2 g, 6.8 mmol), and triethylamine (0.84 g, 8.8 mmol) were combined in a round-bottomed three-necked flask and the catalyst was added. The flask was connected to a condenser and the mixture heated to boiling in an oil bath keeping a slight nitrogen pressure on the flask. When the boiling point stopped increasing (from 96 to 106 °C), the reaction mixture was cooled and diluted with water and ether. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and distilled under reduced pressure. After purification by column chromatography (eluent C), **31a** (1.0 g, 66% yield) was obtained as a pale yellow oil: TLC (eluent C R_f 0.5); IR ($CHCl_3$) 3020, 2951, 1716 cm^{-1}; UV: λ_{max} (log ϵ) (MeOH) 226 (3.38), 314 (2.51); ^{1}H NMR ($CDCl_3$) δ 8.20 (d, J = 16.6 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.46 (m, 2H), 7.30 (d, J = 8.4 Hz, 1H), 6.40 (d, J = 16.6 Hz, 1H), 3.89 (s, 3H), 2.50 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 166.77, 142.58, 133.84, 131.95, 131.27, 130.50, 128.43, 128.13, 127.84, 126.36, 125.00, 124.35, 51.52, 20.73. Anal. Calcd for $C_{15}H_{14}O_2$ (226.27): C, 79.61; H, 6.24. Found: C, 79.41; H, 6.18.

31a (1 g, 4.4 mmol) in ethanol (50 mL) was hydrogenated at 1 atm and 23 °C in the presence of 10% palladium on charcoal (0.42 g). After 4 h the catalyst was filtered off and KOH (0.5 g) was added. The reaction mixture was then heated to reflux for 30 min, the solvent evaporated, and the residue dissolved in water and extracted with ether. After acidification of the aqueous layer and extraction with ether, the solvent was removed, furnishing **32a** as a white solid (90% yield): mp 122 °C; TLC (eluent A, R_f 0.5); IR ($CHCl_3$) 3223, 1711 cm^{-1}; UV λ_{max} (log ϵ) (MeOH) 228 (4.90), 284 (3.73); ^{1}H NMR ($CDCl_3$) δ 7.98 (d, J = 9 Hz, 1H), 7.78 (t, J = 9 Hz, 2H), 7.50 (t, J = 9 Hz, 1H), 7.34 (t, J = 9 Hz, 1H), 7.27 (d, J = 9 Hz, 1H), 3.45 (t, J = 8.4 Hz, 2H), 2.67 (t, J = 8.4 Hz, 2H), 2.54 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 178.82, 133.26, 133.06, 132.68, 131.83, 129.18, 128.76, 126.80, 126.32, 124.70, 122.99, 34.02, 23.80, 19.98. Anal. Calcd for $C_{14}H_{14}O_2$ (214.26): C, 78.48; H, 6.59. Found: C, 78.44; H, 6.58.

26: yellow solid (73% yield); mp 31−33 °C; TLC (eluent B, R_f 0.6).

1-Diazo-4-(1-methyl-2-naphthyl)-2-butanone (34). 3-(1-Methyl-2-naphthyl)acrylic acid, methyl ester (**31b**) was prepared by the Heck reaction as described above for **31a**: yellow solid (71% yield); mp 49−52.5 °C; TLC (eluent C, R_f 0.5); IR ($CHCl_3$) 2966, 1715 cm^{-1}; UV λ_{max} (log ϵ) (MeOH) 218 (2.72), 236 (2.76), 274 (3.18), 312 (3.01); ^{1}H NMR ($CDCl_3$) δ 8.32 (d, J = 15.8 Hz, 1H), 8.12 (m, 1H), 7.82 (m, 1H), 7.65 (m, 2H), 7.53 (m, 2H), 6.46 (d, J = 15.8 Hz, 1H), 3.85 (s, 3H), 2.78 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 167.56, 143.07, 134.70, 134.06, 132.84,

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130.10, 128.5, 126.67, 126.51, 124.87, 123.55, 119.40, 51.70, 14.52. Anal. Calcd for $C_{15}H_{14}O_2$ (226.10): C, 79.61; H, 6.24. Found: C, 79.51; H, 6.18.

Catalytic hydrogenation and subsequent hydrolysis (see **32a**) afforded **32b**: white solid (72% yield); mp 88−90 °C; TLC (eluent A, R_f 0.5); IR ($CHCl_3$) 3223, 2966, 1711 cm^{-1}; UV λ_{max} (log ϵ) (MeOH); ^1H NMR ($CDCl_3$) δ 8.06 (d, J = 8.4 Hz, 1H), 7.82 (dd, J = 1.5, 7.6 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.50 (td, J = 1.5, 7.6 Hz, 2H), 7.33 (d, J = 8.4 Hz, 1H), 3.21 (t, J = 7.6 Hz, 2H), 2.68 (s, 3H), 2.68 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 178.77, 136.00, 133.00, 128.41, 127.73, 126.34, 125.95, 125.00, 123.97, 35.16, 29.21, 14.21. Anal. Calcd for $C_{14}H_{14}O_2$ (214.26): C, 78.48; H, 6.59. Found: C, 78.40; H, 6.64.

34: yellow solid in 76% yield; mp 57.5−59.5 °C; TLC (eluent B, R_f 0.6).

1-Diazo-4-(7-methoxy-1-methyl-2-naphthyl)-2-butanone (37). A suspension of 7-methoxy-1-tetralone (**46**) (12 g, 68 mmol), sodium hydride (60%, 3.56 g, 89 mmol), and diethyl carbonate (32 g, 27 mmol) was refluxed for 1 h and then poured into ice−water, and the solution, adjusted with concentrated HCl to pH 1.5, was extracted with ether. After evaporation of the solvent, the residue was column chromatographed (eluent E) to give pure 2-(ethoxycarbonyl)-7-methoxy-1-tetralone (**47**) (13 g, 83% yield): mp 36−37.5 °C; TLC (eluent E, R_f 0.5); IR ($CHCl_3$) 1736, 1682 cm^{-1}; UV λ_{max} (log ϵ) (MeOH) 226 (4.30), 292 (4.10), 304 (4.10), 336 (4.09); ^1H NMR ($CDCl_3$) δ 7.49 (d, J = 2.6 Hz, 1H), 7.14 (d, J = 8.3 Hz, 1H), 7.06 (dd, J = 2.6; 8.3 Hz, 1H), 4.26 (q, J = 7 Hz, 2H), 3.81, (s, 3H), 3.55 (dd, J = 4.7; 10 Hz, 1H), 2.94 (m, 2H), 2.50−2.40 (m, 1H), 2.30−2.20 (m, 1H), 1.33 (t, J = 7 Hz, 3H). Anal. Calcd for $C_{14}H_{16}O_4$ (248.10): C, 67.71; H, 6.50. Found: C, 67.58; H, 6.46.

47 (13 g, 52 mmol) and ethyl acrylate (6.84 g, 68 mmol) were added to an ethanolic solution (500 mL) of sodium ethoxide prepared from 362 mg (0.15 mmol) of sodium. The reaction mixture was kept under stirring at room temperature for 4 h and then poured into ice−water. After evaporation of the ethanol, the residue was extracted with ether and the solvent evaporated *in vacuo*. The crude diester was dissolved in 1.5 N aqueous KOH (200 mL, H_2O−dioxane 2:1) and the solution heated under reflux for 8 h. After the pH was adjusted to 1.5, extraction with ether and evaporation of the solvent afforded pure **48** as a white solid (9.18 g, 95%): mp 112.5−113.5 °C; TLC (eluent A, R_f 0.5); IR ($CHCl_3$) 2966, 1713, 1672 cm^{-1}; UV λ_{max} (log ϵ) (MeOH) 222 (4.34), 252 (3.97), 320 (3.49); ^1H NMR ($CDCl_3$) δ 7.48 (d, J = 2.8 Hz, 1H), 7.13 (d, J = 8.6 Hz, 1H), 7.03 (dd, J = 2.8, 8.6 Hz, 1H), 2.94 (dd, J = 4.7, 7.4 Hz, 2H), 2.55 (m, 1H; t, J = 7.4 Hz, 2H), 2.28 (m, 2H), 1.88 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 199.58, 179.48, 158.28, 136.36, 133.06, 129.82, 121.62, 109.35, 46.39, 31.58, 28.92, 27.68, 24.84. Anal. Calcd for $C_{14}H_{16}O_4$ (248.10): C, 67.71; H, 6.50. Found: C, 67.68; H, 6.53.

In a round-bottomed three-necked flask, under a nitrogen atmosphere, methylmagnesium iodide was prepared in the usual manner from 200 mg (0.83 mmol) of I_2-activated magnesium and 1.2 g (0.81 mol) of CH_3I in 10 mL of anhydrous ether. **48** (0.8 g, 0.32 mol) in 6 mL of anhydrous ether was added dropwise at a rate so as to mantain a gentle reflux. When addition was completed, the reaction mixture was refluxed for additional 90 min and then cooled and quenched with 9 mL of ice and 6 mL of 20% H_2SO_4 to give a lime-colored slurry. After removal of the solvent, 20% H_2SO_4 (6 mL) was added and the mixture heated under a vigorous reflux for 15−20 min. The reaction mixture was then cooled and extracted three times with ether. The combined organic portions were washed with 10 mL of a saturated $NaHCO_3$ solution and the acqueous phase was adjusted to pH 1−2 with concentrated hydrochloric acid. The white precipitated was extracted with ether, dried, and evaporated to give 0.7 g (0.29 mmol) of pure 3-(7-methoxy-1-methyl-3,4-dihydro-2-naphthyl)propionic acid (**49**) as a light pink solid in 88% yield: TLC (eluent A, R_f 0.5); IR ($CHCl_3$) 2934, 2253, 1709 cm^{-1}; UV λ_{max} (log ϵ) (MeOH) 222 (4.31), 262 (3.89), 302 (3.53); ^1H NMR ($CDCl_3$) δ 7.05 (d, J = 8 Hz, 1H), 6.85 (d, J = 2.5 Hz, 1H), 6.70 (dd, J = 2.5; 8 Hz, 1H), 3.85 (s, 3H), 2.75−2.54 (m, 4H), 2.55 (m, 2H), 2.25 (m, 2H), 2.05 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 179.59, 158.31, 137.92, 134.52, 127.82, 127.48, 126.71, 110.27, 109.86, 55.28, 32.83, 29.41, 28.55, 27.61, 14.00. Anal. Calcd for $C_{15}H_{18}O_3$ (246.13): C, 73.13; H, 7.37. Found: C, 73.00 ; H, 7.41.

A mixture of **49** (3.8 g, 15.3 mmol) and DDQ (3.46 g, 16.2 mmol) in benzene (80 mL) was stirred at room temperature for 30 min. The mixture was diluted with ether, washed with aqueous ammonium chloride, water, and brine, and then dried over anhydrous sodium sulfate and evaporated to dryness. The crude product was purified by flash chromatography to give 3.3 g (88% yield) of pure 3-(7-methoxy-1-methyl-2-naphthyl)propionic acid (**50**): mp 131−131.5 °C from diethyl ether; TLC (eluent A, R_f 0.5); IR ($CHCl_3$) 2934, 1697 cm^{-1}; UV λ_{max} (log ϵ) (MeOH) 234 (4.93), 280 (3.65), 330 (3.12); ^1H NMR ($CDCl_3$) δ 7.72 (t, J = 8.6 Hz, 1H), 7.61 (d, J = 8.6 Hz, 1H), 7.31 (d, J = 2.2 Hz, 1H), 7.20 (d, J = 8.6 Hz, 1H), 7.14 (dd, J = 2.2, 8.6 Hz, 1H), 3.96 (s, 3H), 3.19 (t, J = 8 Hz, 2H), 2.70 (t, J = 8 Hz, 1H), 2.62 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 178.54, 157.86, 135.68, 134.12, 129.91, 129.67, 127.92, 126.04, 125.42, 117.21, 103.10, 55.28, 35.16, 29.34, 14.34. Anal. Calcd for $C_{15}H_{16}O_3$ (244.1): C, 73.74; H, 6.61. Found: C, 73.62; H, 6.54.

37: yellow solid (75% yield); mp 94.5−96 °C; TLC (eluent B, R_f 0.6).

$Rh_2(AcO)_4$ Decomposition of Diazo Ketones. Typical Procedure. In a round-bottomed two-necked flask, 12 mg of $Rh_2(OAc)_4$ was dissolved in 36 mL of dry CH_2Cl_2, under a nitrogen atmosphere and with magnetic stirring. The flask was protected from the action of light and cooled at 0 °C. The diazo ketone (0.42 mmol) was dissolved in 24 mL of dry CH_2Cl_2 and added dropwise very slowly. The mixture was then kept at rt for 2 h more and then diluted with 20 mL of CH_2Cl_2 and washed with water. The organic layer was dried over anhydrous sodium sulfate and evaporated to give a crude product. This was then flash chromatographed eluting with systems D or F to afford the pure reaction product(s).

Tetracyclo[8.4.0.0^{1,11}.0^{2,7}]tetradeca-2,4,6,8-tetraen-12-one (11): Pale yellow oil (78% yield from **10**); TLC (eluent D, R_f 0.34).

10-Methoxytetracyclo[8.4.0.0^{1,11}.0^{2,7}]tetradeca-2,4,6,8-tetraen-12-one (14): pale yellow oil (70% yield from **13**); TLC (eluent D, R_f 0.31).

10-Methyltetracyclo[8.4.0.0^{1,11}.0^{2,7}]tetradeca-2,4,6,8-tetraen-12-one (27): pale yellow oil (80% yield from **26**); TLC (eluent D, R_f 0.32); IR ($CHCl_3$) 2930, 1711 cm^{-1}; UV λ_{max} (log ϵ) (MeOH) 232 (4.37), 272 (3.89); EIMS *m/e* (rel intensity) 210 (M^+, 67), 195 (15), 182 (68), 181 (100); ^1H NMR ($CDCl_3$) δ 7.69 (d, J = 7.7 Hz, H-8), 7.30 (td, J = 1.3; 8 Hz, H-6), 7.25 (d, J = 8 Hz, H-5), 7.19 (td, J = 1.3; 7.7 Hz, H-7), 6.42 (d, J = 9 Hz, H-9), 6.16 (d, J = 9 Hz, H-10), 3.20 (td, J = 5.6; 13.6 Hz, H-3), 2.55 (m, H-3), 2.30−2.05 (m, H_2-4), 1.45 (s, Me-11), 1.06 (s, H-1); ^1H NOE from H-1 to Me (0.5%); from Me to H-1 (0.8%) and to H-10 (2.7%); from H-10 to Me (0.6%); ^{13}C NMR ($CDCl_3$) δ 214.97 (C-2), 134.24, 132.61 (C-10), 130.66, 128.18 (C-5), 127.55 (C-6), 126.44 (C-7), 125.18 (C-9, C-8), 43.62, 39.21 (C-1), 37.32 (C-4), 35.28, 21.37 (C-3), 16.92 (C-11). Anal. Calcd for $C_{15}H_{14}O$ (210.10): C, 85.67; H, 6.72. Found: C, 85.71; H, 6.74.

10-Methyltetracyclo[8.4.0.0^{1,11}.0^{4,9}]tetradeca-2,4,6,8-tetraen-12-one (35): pale yellow oil (14% yield from **34**); TLC (eluent D, R_f 0.31).

10-Methyl-3,4-dihydroanthracen-2(*1H*)-one (36): white solid (28% yield from **34**); mp 120−121 °C from hexane−acetate 2:1; TLC (eluent D, R_f 0.38).

7-Methoxy-10-methyltetracyclo[8.4.0.0^{1,11}.0^{4,9}]tetradeca-2,4,6,8-tetraen-12-one (38): pale yellow oil (11% yield from **37**); TLC (eluent F, R_f 0.29).

6-Methoxy-10-methyl-3,4-dihydroanthracen-2(*1H*)-one (39): white solid (52% yield from **37**); mp 135−136 °C from hexane−acetate 2:1; TLC (eluent F, R_f 0.38); IR ($CHCl_3$) 2361, 1707 cm^{-1}; UV λ_{max} (log ϵ) (MeOH) 236 (4.91), 280 (3.70), 334 (3.26); EIMS *m/e* (rel intensity) 240 (M^+, 100), 225 (10), 212 (22), ^1H NMR ($CDCl_3$) δ 7.67 (d, J = 8.8 Hz, H-8), 7.42 (s, H-9), 7.28 (d, J = 2.4 Hz, H-5), 7.13 (dd, J = 2.4; 8.8 Hz, H-7), 3.95 (s, MeO), 3.72 (s, H_2-1), 3.27 (t, J = 6.6 Hz, H_2-4), 2.64 (s, Me), 2.57 (t, J = 6.6 Hz, 2H); ^1H NOE from Me to H_2-4 (3%) and to H-5 (7%); from H-5 to Me (2.6%) and to MeO (2.1%); from H_2-1 to H-9 (6.4%); from H-9 to H-1 (2.8%) and to H-8 (5.6%); from H-8 to H-9 (3%) and to H-7 (6.9%); from H-7 to

H-8 (6.6%); ^{13}C NMR ($CDCl_3$) δ 210.82 (C-2), 157.70 (C-6), 133.45, 132.98, 129.00, 128.84, 129.47 (C-8), 128.32, 124.75 (C-9), 117.53 (C-7), 103.28 (C-5), 55.29 (C-12), 46.36 (C-1), 38.30 (C-3), 25.26 (C-4), 14.67 (C-11). Anal. Calcd for $C_{16}H_{16}O_2$ (240.12): C, 79.96; H, 6.72. Found: C, 80.00; H, 6.76.

TFA Decomposition of Cyclopropane Derivatives. Typical Procedure. In a round-bottomed two-necked flask, the tetracyclic ketone (0.41 mmol) was dissolved in 20 mL of CH_2Cl_2, under magnetic stirring. After addition of TFA (5 μL) the mixture was kept under magnetic stirring for 10 min at rt and then washed with water (2 × 10 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to give a residue which was flash chromatographed by eluting with systems A or B or D to give the pure product(s).

3,4-Dihydrophenanthren-2(*1H*)one (12): yellow solid (95.5% yield from **11**); mp 65.2 °C (lit.[18] mp 61−62 °C); TLC (eluent A, R_f 0.78).

Naphthalen-2(*1H*)-one-1-spiro-(1′-cyclopentan-3′-one) (15): colorless solid (78% yield from **14**); mp 71−72 °C; TLC (eluent C, R_f 0.31).

4a-Methyl-4,4a-dihydrophenanthren-2(*3H*)-one (28): pale yellow solid (44% yield from **27**); mp 98 °C from hexane (lit.[12,24a] mp 98−99 °C); TLC (eluent E, R_f 0.26).

10a-Methyl-1,10a-dihydrophenanthren-3(*2H*)-one (29): white solid (47% yield from **27**); mp 99−100 °C from hexane; TLC (eluent E, R_f 0.29); IR ($CHCl_3$) 2928, 1653 cm^{-1}; UV λ_{max} (log ϵ) (MeOH) 258 (4.38), 306 (3.96), 348 (3.68); EIMS *m/e* (rel intensity) 210 (M^+, 69), 195 (37), 182 (53), 177 (100); ^{1}H NMR ($CDCl_3$) δ 7.60 (d, J = 7.7 Hz, H-5), 7.38 (t, J = 7.7 Hz, H-6), 7.26 (td, J = 1.5; 7.7 Hz, H-7), 7.13 (d, J = 7.7 Hz, H-8), 6.43 (d, J = 9.6 Hz, H-9), 6.34 (s, H-4), 5.86 (d, J = 9.6 Hz, H-10), 2.64−2.55 (m, H_2-2), 2.21 (td, J = 5; 13.6 Hz, H-1), 2.01 (ddd, J = 1.9; 5; 13.6 Hz, H-1), 1.27 (s, Me-11); ^{1}H NOE from H-4 to H-5 (6.5%); from H-5 to H-4 (8.6%) and to H-6 (-6%); from H-8 to H-7 (-5%) and to H-9 (2.8%); from H-9 to H-8 (2.7%) and to H-10 (3.7%); from H-10 to H-9 (3.3%) and to Me (1.1%); from Me to H-10 (3.7%) and to H-1 (δ 1.99, 4%); ^{13}C NMR ($CDCl_3$) δ 198.60 (C-3), 163.54, 138.00 (C-10), 134.00, 131.24 (C-6), 128.06 (C-7), 129.67, 126.97 (C-8), 125.46 (C-5), 124.15 (C-9), 122.74 (C-4), 37.26, 35.18 (C-1), 34.01 (C-2), 24.11 (C-11). Anal. Calcd for $C_{15}H_{14}O$ (210.10): C, 85.67; H, 6.72. Found: C, 85.70; H, 6.75.

6-Methoxy-10a-methyl-1,10a-dihydrophenanthren-3(*2H*)-one (51): yellow oil (75% yield from **38**); TLC (eluent E, R_f 0.29).

6-Methoxy-1,1,10-trimethyl-3,4-dihydroanthracen-2(*1H*)-one (52). Methyl iodide (0.118 g, 0.83 mmol) was added slowly, under magnetic stirring, to a solution of **39** (0.1 g, 0.42 mmol) in dry *t*-BuOH (5 mL) containing *t*-BuOK (0.93 g, 0.84 mmol). The reaction mixture was left to react at rt for 10 min and then poured into 20 mL of water. After neutralization with dilute HCl and extraction with ether, the organic layer was washed with water, dilute sodium hydroxide, and water again. Drying over anhydrous Na_2SO_4 and removal of the solvent furnished the crude product as a dark oil. This was purified by flash chromatography using eluent G to give pure **52** (0.98 g, 88% yield) as a yellow solid: mp 79.5−80 °C; TLC (eluent G, R_f 0.5); IR ($CHCl_3$) 2970, 1713 cm^{-1}; UV λ_{max} (log ϵ) (MeOH) 238 (4.89), 282 (3.62); EIMS *m/e* (rel intensity) 268 (M^+, 100), 253 (60), 225 (92); ^{1}H NMR ($CDCl_3$) δ 7.71 (d, J = 9 Hz, H-8), 7.65 (s, H-9), 7.28 (d, J = 2.1 Hz, H-5), 7.13 (dd, J = 2.1; 9 Hz, H-7), 3.95 (s, MeO-12), 3.30 (t, J = 7.3 Hz, H_2-4), 2.72 (t, J = 7.3 Hz, H_2-3), 2.62 (s, Me-11), 1.53 (s, Me-13, Me-14); ^{1}H NOE from Me to H_2-4 (4.5%) and to H-5 (9.2%); from Me-13,14 to H-9 (14.7%); ^{13}C NMR ($CDCl_3$) δ 214.89 (C-2), 157.77 (C-6), 139.69, 132.13, 132.12, 129.90 (C-8), 129.10, 128.10, 122.98 (C-9), 117.55 (C-7), 102.66 (C-5), 55.25 (C-12), 48.17, 37.37 (C-3), 27.21 (C-13, C-14), 25.57 (C-4), 14.77 (C-11). Anal. Calcd for $C_{18}H_{20}O_2$ (268.15): C, 80.55; H, 7.52. Found: C, 80.44; H, 7.48.

6-Methoxy-1,1,10-trimethyl-1,2,3,4-tetrahydroanthracene (53). *p*-Toluenesulfonohydrazide (119 mg, 0.64 mmol) was added to a stirred solution of **52** (86 mg, 0.32 mmol) in acetic acid (5 mL). The mixture was manteined for 2 h at rt and then diluted with water (8 mL). The precipitate was isolated by suction, washed with water, and dried to give the tosylhydrazone (137 mg, 98% yield): TLC (eluent G, R_f 0.28); IR ($CHCl_3$) 1714, 1628 cm^{-1}; UV λ_{max} (log ϵ) (MeOH) 238 (4.92), 334 (3.18); EIMS *m/e* (rel intensity) 436 (M^+, 25), 281 (20), 266 (20), 252 (100). Anal. Calcd for $C_{25}H_{28}N_2SO_3$ (436.57): C, 68.78; H, 6.46; N, 6.42; S, 7.34. Found: C, 68.80; H, 6.47; N, 6.48.

A stirred solution of the tosylhydrazone prepared above (109 mg, 0.25 mmol), $NaBH_3CN$ (1 mmol), and *p*-toluensulfonic acid (12.5 mg) in 4 mL of a 1:1:2 mixture of DMF−sulfolane−cyclohexane was heated at 110 °C. Additonal portions of $NaBH_3CN$ (1 mmol) were added every 2 h and for three times and heating was continued. Upon completion (monitored by TLC) the reaction mixture was diluted with water and the layers were separated. The organic phase was dried over anhydrous Na_2SO_4 and the solvent removed by evaporation to give a crude product. This was purified by flash chromatography using eluent G to furnish **53** as a colorless solid in 85% yield: mp 111 °C from hexane (lit.[21c] mp 110 °C; lit.[21d] mp 112−113 °C).

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Supporting Information Available: Experimental data for compounds **11**−**15**, **26**, **28**, **34**−**38**, and **51** and ^{1}H and ^{13}C NMR spectra for compounds **11**, **14**, **15**, **27**−**29**, **35**, **36**, **38**, **39**, and **51**−**53** (31 pages). This material is contained in 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.

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