Enthalpy and Entropy of Conjugative Interaction in a Nearly Coplanar Styrene and Cinnamyl Radical

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Abstract: Conjugative interaction in styrenes designed to constrain the dihedral angle between the planes of the phenyl and olefinic groups near to coplanarity (21° by X-ray) is greater by 0.7 kcal mol^{-1} than that in a styrene in which the phenyl group is unconstrained (ad libitum) (−35° by MM2 molecular mechanical calculation). Conjugative interaction in a cinnamyl radical similarly constrained to maintain the phenyl and allyl moieties nearly coplanar (15° by MM2) is greater by 1.1 kcal mol^{-1} than in a cinnamyl radical in which the phenyl group is ad libitum. Efforts to separate the contribution of π-electron delocalization from the nonbonded steric factor by employing MM2 calculations proved quantitatively unsatisfactory.

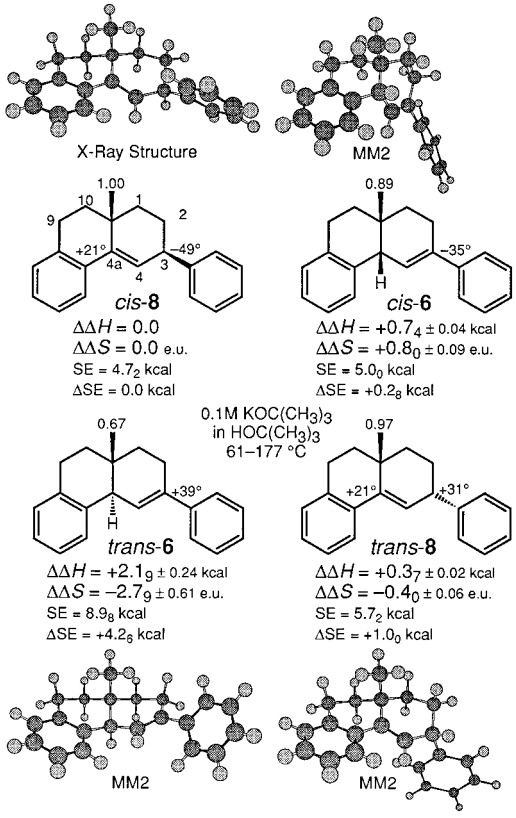
Conjugative interaction between phenyl group and olefin in styrenes has been found to weaken as steric factors cause an increase in dihedral angle.[1] A phenyl group free to assume whatever dihedral (torsional) angle optimizes interaction (ad libitum) varies in conjugative interaction vis-à-vis alkyl from 2.5 kcal mol^{-1} in unhindered trans-β-substituted styrenes, through 1.1 kcal mol^{-1} in cis-β-substituted styrenes to 0.0 kcal mol^{-1} in an α-substituted styrenes. In this paper, an effort is made to enforce near coplanarity by incorporating phenyl group and double bond into a bicyclic system.

Conjugative interaction between a phenyl group and the π-system of an allyl radical is closely related. How such interaction in the cinnamyl radical compares with that of the olefinic group in pentadienyl is of fundamental theoretical interest. Here, too, elucidation of the change in the magnitude of the interaction as the dihedral angle approaches zero or coplanarity is the focus.

Results and Discussion

Coplanarity in Conjugative Interaction in Styrenes. To explore the possibility of enforcing coplanarity in a styrene, compounds of the type **6** and **8** shown in Chart 1 have been selected. The three-atom system classically used for the estimation of free energy of conjugation is represented in these compounds by carbon atoms 4a, 4, and 3. Synthesis, although uncomplicated, contains a delightful interplay of kinetic and thermodynamic control. Following literature procedures,[2,3] preparation begins with α-tetralone and proceeds through compounds **1** and **2** to racemic **3** (Scheme 1). Reduction over palladium on charcoal affords a mixture of four stereoisomers (**4**), one of which, isolated in pure form, mp 112 °C, can be oxidized with chromic acid to ketone **5** of mp 72 °C. Treatment with phenylmagnesium bromide affords a pair of phenylcarbinols (not separated), which, on being heated with *p*-toluenesulfonic acid, are dehydrated to a pair of olefins

Chart 1



consisting for the most part of a crystalline isomer, mp 116 °C. Its structure has been determined by X-ray crystallographic analysis to be *trans*-**7** (Scheme 2).[4] Acid-catalyzed equilibration confirms an equilibrium consisting of 96% of *trans*-**7** and 4% of *trans*-**6**. That the integrity of the trans configuration of the hexalin ring has not been compromised in this equilibration (not to be expected on mechanistic grounds) is confirmed by repeating the sequence starting from the mixture of carbinols

(1) Doering, W. v. E.; Benkhoff, J.; Carleton, P. S.; Pagnotta, M. *J. Am. Chem. Soc.* **1997**, *119*, 10947−10955.

(2) Cainelli, G.; Panunzio, M.; Umani-Ronchi, A. *Tetrahedron Lett.* **1973**, 2491−2494.

(3) DeBoer, C. D. *J. Org. Chem.* **1974**, *39*, 2426−2327.

(4) Staples, R. J.; Doering, W. v. E.; Benkhoff, J. *Z. Krystallogr.* **1997**, *212*, 435−436.

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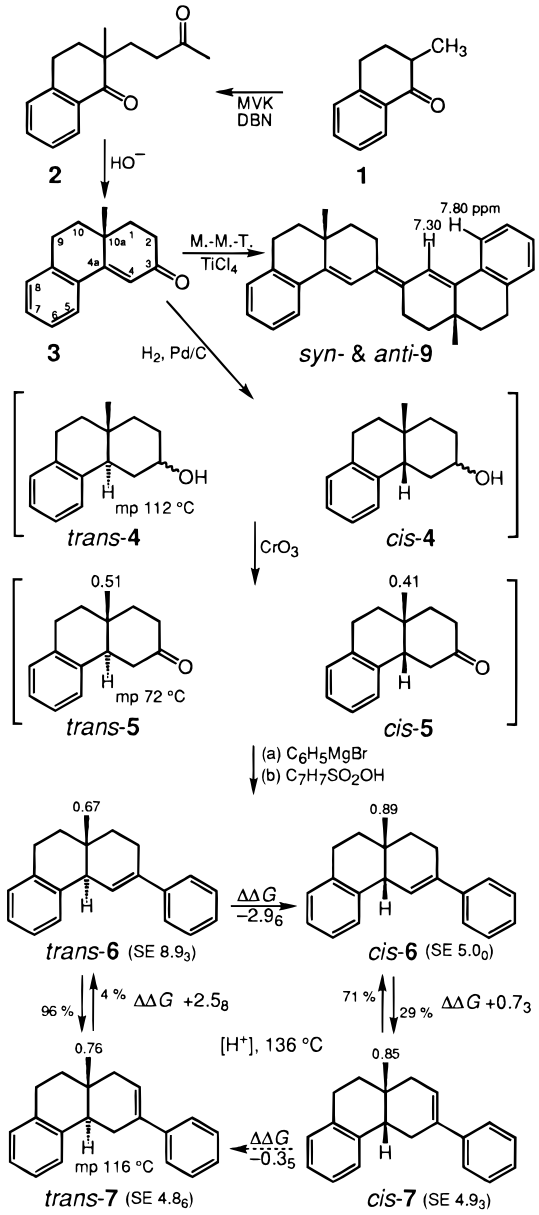
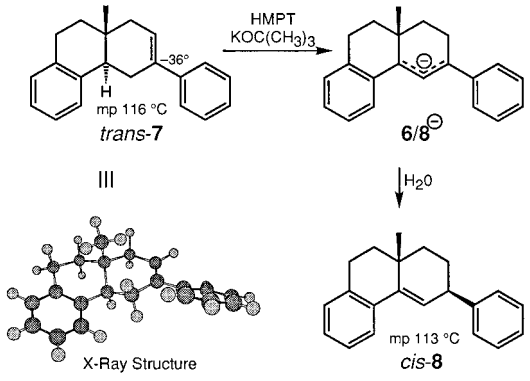
Scheme 1



Scheme 2



4. Along with *trans*-**6** and *trans*-**7**, two additional compounds, reasonably presumed both to have the cis configuration, can be identified in the NMR spectrum. Parenthetically, the values of $\Delta\Delta G$ at 136 °C for the pairs, *trans*-**6** to *trans*-**7**, and *cis*-**6** to *cis*-**7**, are −2.6 and +0.7 kcal mol^{-1}, respectively. These values compare with the corresponding differences in "steric energy" (ΔSE) calculated by MM2 (see below) of -4.0_7 and -0.0_7 kcal mol^{-1}, respectively.

Table 1. Ratios among *cis*-**8**, *cis*-**6**, *trans*-**8**, and *trans*-**6** at Equilibrium at Various Temperatures Relative to *cis*-**8**

T, °C	$K_{cis-8/trans-8}$	$K_{cis-8/cis-6}$	$K_{cis-8/trans-6}$
61.0	2.14	2.05	102.0
97.3	2.04	1.79	86.3
111.0	2.00	1.77	70.2
121.1	1.97	1.75	71.2
136.3	1.93	1.65	68.4
137.2	1.93	1.66	57.5
152.8	1.90	1.59	51.7
165.0	1.86	1.55	46.7
177.5	1.87	1.54	46.4

Entry into conjugated compounds of type **8** is made by treating the readily accessible *trans*-**7** with a strongly basic system consisting of potassium *tert*-butoxide in hexamethylphosphorictriamide (HMPT) scrupulously free of water and *tert*-butyl alcohol. Quenching the deep purple solution with water produces in high yield a crystalline material, mp 113 °C, the structure of which is determined by X-ray crystallographic analysis to be that of *cis*-**8**.[5]

That this catalytic system is too strongly basic to be suitable for the determination of the temperature-dependence of the equilibria in Chart 1 is demonstrated by quenching the purple solution with deuterium oxide. The resulting samples of *cis*-**8** and *cis*-**6** contain 76 and 71% of deuterium, respectively, while recoverd *trans*-**7** contains less than 1% deuterium. These observations invite the conclusions that 70−75% of *cis*-**8** and *cis*-**6** is present as the stable, common anion, **6/8** (Scheme 2), and that a more weakly basic catalytic system will not only suffice to establish equilibria among the neutral isomers but will not lead to kinetic contamination from neutralization of a common anion. In practice, replacement of HMPT as solvent by anhydrous *tert*-butyl alcohol meets the requirements. In other respects, the experimental procedure is the same as that previously described in detail.[1]

Equilibrium among the four isomers is established cleanly without the formation of disturbing byproducts. Good fortune has made quantitative discrimination among these isomers easy, thanks to the sharp singlets of their bridgehead methyl groups, the chemical shifts (δ) of which are noted in Scheme 1 and Chart 1. Ratios of the most stable isomer, *cis*-**8**, to the other three at various temperatures are given in Table 1. Note that the analytical error associated with *trans*-**6** is inevitably larger but still of a magnitude compatible with useful conclusions. A plot of the experimental data, given in Figure S1 of Supporting Information, as the natural logarithm of the ratios of the concentration of an individual isomer to the sum of all four isomers (in %) against the reciprocal of temperature (K^{-1}) provides slopes and intercepts, "ΔH" and "ΔS", relatable to $\Delta\Delta H$ and $\Delta\Delta S$, each with its own standard deviation. These values are recorded in Chart 1, relative to *cis*-**8** as zero.

Among the four isomers, the styrene systems in *cis*-**8** and *trans*-**8** are more nearly coplanar than the similarly substituted, ad libitum styrenes, *cis*- and *trans*-**6**. From the X-ray crystallographic analysis of its structure, the styrene system in *cis*-**8** has a dihedral angle of 21°, further from coplanarity than hoped for at the inception of this work. By comparison, the dihedral angle in *trans*-**7**, alone among the four ad libitum styrenes to have its structure determined by crystallographic analysis, is −36°. For the rest, we find molecular mechanics, as developed

(5) Staples, R. J.; Doering, W. v. E.; Benkhoff, J. *Z. Krystallogr*. **1997**, *212*, 433−434.

by Allinger[6] and made available by Cambridge Software,[7] a satisfying way of resolving conformational questions. In its application, painstaking care involving systematic variation of initial conformations has been taken in an effort to avoid entrapment in local minima.[8] By MM2, not only is the styrene dihedral angle in *cis*-**8** reproduced (21°) but also is the entire conformation. Similarly well reproduced is the dihedral angle in *trans*-**7** (−36°) and its conformation (global minimum). The remaining MM2-calculated, styrene dihedral angles in the global minima follow: *trans*-**8**, 21°; *cis*-**7**, 36°; *cis*-**6**, −35°; *trans*-**6**, +39°.

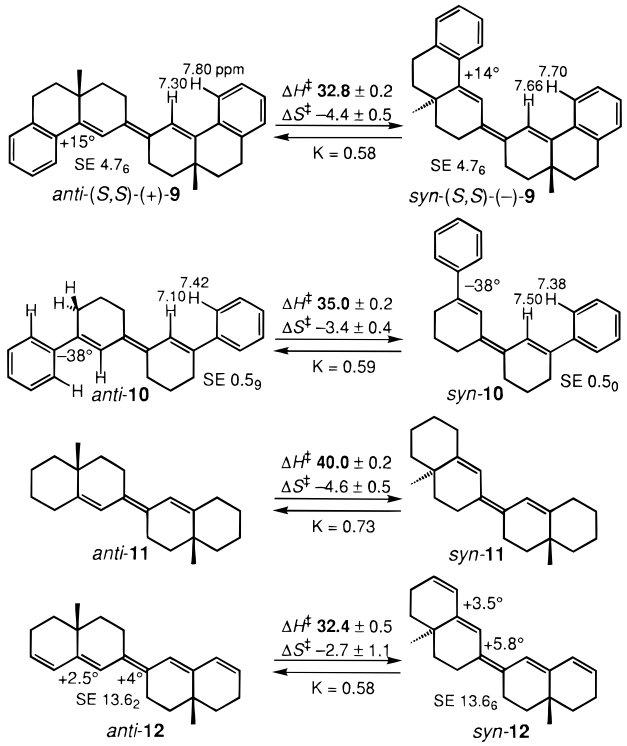
Empirically, the Δ^1 isomers, *cis*-**6** and *trans*-**6**, have a higher enthalpy of formation than their corresponding Δ^{8a} isomers, *cis*-**8** and *trans*-**8**, by 0.7_4 and 1.8_2 kcal mol^{-1}, respectively. Were it not for steric factors, these values might be expected to be very nearly equal. To estimate any differences in the contribution of the π-electron component, correction for the steric component is essential.

Attempts to make this correction by application of molecular mechanics have not succeeded at the required level of accuracy. The compounds in this work seem as favorable as can be imagined. The pairs, *cis*- and *trans*-**6** and *cis*- and *trans*-**8**, are each in fact "isoBensonian"; that is, they are constituted of identical sets of group equivalent values and therefore have identical "Bensonian" heats of formation. The pairs, *cis*-**6** and *cis*-**8** and *trans*-**6** and *trans*-**8**, almost qualify! Their difference is likely small but cannot be estimated by the Benson method because of the lack of one (empirically based) group equivalent value: [C−(H)$_2$(C)$_2$ = −4.93] and [C−(C$_d$)(C)$_3$ = ?] for compounds of type **8** and [C−(C$_d$)(C)(H)$_2$ = −4.76] and [C−(C)$_4$ = +0.50] for compounds of type **6**.

The steric energy of the global minimum calculated by MM2 for *trans*-**6** (+8.9_8 kcal mol^{-1}) is so much larger than that calculated for *trans*-**8** (+5.7_2 kcal mol^{-1}) that any effort to extract a quantitative estimate of π-electron delocalization energy is problematic, particularly in the face of the large experimental uncertainty in the relative enthalpy of formation of *trans*-**6**. An uncritical comparing of the calculated difference in steric energy of 3.2_6 kcal mol^{-1} to the experimental difference of 1.8_2 kcal mol^{-1} leads to the conclusion that the difference in π-electron delocalization amounts to -1.4_4 kcal mol^{-1} ($1.8_2 - 3.2_6$) in favor of the ad libitum styrene, *trans*-**6**. A similar procedure applied to *cis*-**6** and *cis*-**8** leads to the conclusion that the difference in π-electron delocalization between ad libitum *cis*-**6** and the more nearly coplanar *cis*-**8** had disfavored *cis*-**6** by +0.4_6 kcal mol^{-1}! These conclusions can scarcely both be true. As a cautionary note, had relative steric energies from MM2 calculations been used as the basis for assignment of structure, *cis*-**6** and *trans*-**8** would have been mistakenly interchanged.

Until either of two things come to pass, molecular mechanical methods reach a level of thermochemical accuracy commensurate with the needs of defining positions of equiilibrium or quantum chemical mechanical methods attain the ability to calculate enthalpies of formation of larger molecules with an accuracy, for example, of $\pm \leq 0.3$ kcal mol^{-1}, the empirical difference of 0.7_4 kcal mol^{-1} in favor of the more nearly planar *cis*-**8** *may* be a qualitative indication of a small increase in delocalization energy as dihedral angle is reduced from ∼35° to 21°.[9] This work, however it may reinforce the view expressed earlier[1] that conjugative interaction be a combination of at least two factors, also illustrates once again the hazards inherent in the time-honored strategy of introducing a structural perturbation for the purpose of exploring a single mechanistic hypothesis only to find that the strategem has led to additional perturbations by inadequately anticipated factors as well!

Scheme 3



Coplanarity in the Cinnamyl Radical. Interaction of phenyl with the allyl radical (the cinnamyl radical) has been elucidated through studies of thermal cis−trans rearrangements about a carbon−carbon double bond in *syn*- and *anti*-bis-(3-phenylcyclohex-2-enylidene) (**10**) by Teles[10] (Scheme 3), and the thermal rearrangements of 1-, 2-, and 3-phenyl- and 1,3- and 3,4-diphenylhexa-1,3-*trans*-5-trienes to the corresponding cyclohexadienes by Wiktor.[11,12] In studies of this type, the rate-determining transition state is assumed to be a 90°-twisted, diradical-like double bond that is stabilized as completely as possible by the energy of π-electron delocalization of a phenyl group free to adopt, ad libitum, its energetically most favorable dihedral angle. It is further assumed that any concomitant reduction in enthalpy of strain in the educt will also contribute to lowering the energy in the transition region. An example is the comparison of *syn*- and *anti*-**10** with the allyl system **11** (Scheme 3).[13] The difference in their enthalpies of activation of 5 kcal mol^{-1} is an indication that an ad libitum phenyl group in the 1-position of a cyclohexene ring is 2.5 kcal mol^{-1} more effective than an alkyl substituent in stabilizing an allyl radical.

(6) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127−8134.

(7) Cambridge Scientific Computing, Inc., 875 Massachusetts Avenue, Cambridge, MA 02139, as "MM2" modified in TINKER by Ponder, J. W. in CSC Chem 3D Plus 3.5.1.

(8) For example, 16 local minima were located for *cis*-**6**, of which that shown in Chart 1 having the lowest steric energy (5.0 kcal mol^{-1}) is taken to be the global minimum.

(9) For the most part, the dihedral angles calculated by MM2 for the global minima are quite soft: ±12−14° corresponding to +0.2 kcal mol^{-1} in steric energy (SE).

(10) Doering, W. v. E.; Birladeanu, L.; Sarma, K.; Teles, J. H.; Klärner, F.-G.; Gehrke, J.-S. *J. Am. Chem. Soc.* **1994**, *116*, 4289−4297.

(11) R. Wiktor in footnote 129, Scheme 17 and Table 39 of ref 12.

(12) Roth, W. R.; Staemmler, V.; Neumann, M.; Schmuck, C. *Liebigs Ann.* **1995**, 1061−1118.

(13) Doering, W. v. E.; Shi, Y.-q.; Zhao, D.-c. *J. Am. Chem. Soc.* **1992**, *114*, 10763−10766.

Table 2. Thermal Interconversion of *anti*- and *syn*-**9** in Toluene-d_8: Equilibrium and Specific Rate Constants and Derived Activation Parameters

T, °C	$10^6\ k_1$, s^{-1} [a]	K
144.5 ± 0.5	6.37 ± 0.07[b]	0.56
144.5 ± 0.5	6.83 ± 0.06[b]	0.56
144.5 ± 0.5	6.62 ± 0.07[c]	0.56
152.3 ± 0.3	14.5 ± 0.2[b]	0.56
152.3 ± 0.3	14.8 ± 0.2[b]	0.56
152.3 ± 0.3	15.4 ± 0.2[c]	0.60
164.7 ± 0.2	42.5 ± 0.9[b]	0.59
164.7 ± 0.2	43.7 ± 0.7[b]	0.59
164.7 ± 0.2	45.6 ± 1.5[c]	0.59
176.9 ± 0.2	118 ± 2[b]	0.60
176.9 ± 0.2	125 ± 1[b]	0.59
176.9 ± 0.2	127 ± 1[c]	0.60
184.3 ± 0.1	229 ± 3[b]	0.61
184.3 ± 0.1	237 ± 1[b]	0.60
184.3 ± 0.1	224 ± 1[c]	0.61

Arrhenius Parameters

$E_a = 33.64 \pm 0.21$ kcal mol^{-1}
$\log A = 12.43 \pm 0.10$

Eyring Parameters

$\Delta H^{\ddagger} = 32.77 \pm 0.21$ kcal mol^{-1}
$\Delta S^{\ddagger} = -4.40 \pm 0.48$ cal mol^{-1} K^{-1} [d]

[a] Calculated by linear regression of the standard expression for reversible first-order reactions. [b] Starting with *anti*-**9**. [c] Starting with *syn*-**9**. [d] Calculated at 164.4 °C.

The styrene system selected to constrain the interacting phenyl group to near coplanarity consists of *anti*- and *syn*-**9** (Schemes 1 and 3). Close analogy to *anti*- and *syn*-**12** permits a straightforward comparison of phenyl and ethenyl. Preparation involves reductive coupling of two molecules of **3** by the method of McMurry, Mukaiyama, and Tyrlik. Applied to racemic **3**, four stereoisomers can be expected by analogy with prior work,[14] whereas applied to a single enantiomer no more than two products can be formed. Accordingly, racemic **3** has been resolved by chromatography on a chiral column. Coupling of the (*S*) isomer produces a mixture of *anti*- and *syn*-(*S*,*S*)-**9**, which has been separated by crystallization.

Rates of thermal equilibration of *anti*- and *syn*-**9** in hexadeuteriobenzene are followed directly by NMR spectroscopy thanks to a satisfactory separation of the resonances of the two pairs of vinyl and ortho protons (noted in Scheme 3). The data acquired at various times and temperatures are collected in the Supporting Information. Specific rate constants are calculated in the usual manner on the basis of the equation governing reversible reactions of the first-order. In that calculation, equilibrium constants are taken from experiment and are thereby fixed rather than treated as a variable, even though statistically a better fit would inevitably have resulted by allowing the equilibrium constant to float. Specific rate and equilibrium constants and derived activation parameters are collected in Table 2.

The more nearly coplanar benzene ring in **9** is more effective (∼1.1 kcal mol^{-1} per phenyl group) at lowering the empirical enthalpy of conjugative interaction than is the ad libitum phenyl group in **10**.[15] In **10**, opposition between the proximate hydrogen atoms of the cyclohexenylidene ring and the *o*-hydrogens of the phenyl group resists attainment of coplanarity and leads to a dihedral angle between benzene ring and double bond calculated by MM2 to be −38°. In **9**, the hexahydronaphthalene system opposes attainment of full coplanarity but nonetheless leads to a smaller dihedral angle of 15°.

The fused benzene ring in **9** is quite similar to the comparable olefinic group in **12** (dihedral angle of 2.5°) in ability to augment enthalpy of stabilization. Both are identically positioned in the same conformationally rigid bicyclic system and both contribute ∼3.5 kcal mol^{-1} to enthalpy of stabilization (cinnamyl and (*E*,*E*)-pentadienyl radical, respectively). Similarly, phenyl (benzyl ∼12 kcal mol^{-1}) and vinyl (allyl ∼13 kcal mol^{-1}) contribute almost identically to the stabilization of the ethyl radical.[16] Unfortunately, the trend in stabilization energy in passing from benzyl to α-methylbenzyl to α,α-dimethylbenzyl has not been elucidated in the literature.

Cinnamyl stabilization has also been evaluated by Wiktor[11] and Roth[12] in a study of the thermal rearrangement of 1-phenylhexa-1-*trans*-3,5-trienes to an equilibrium mixture of phenylcyclohexadienes. Activation parameters determined between 245 and 309 °C are $\Delta H^{\ddagger} = 36.9 \pm 0.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = -8.75 \pm 1.5$ e.u. Comparison with the enthalpy of activation of hexatriene ($\Delta H^{\ddagger} = 43.2 \pm 1.2$ kcal mol^{-1}, $\Delta S^{\ddagger} = -2.7 \pm 2.2$ e.u.,[17] and $\Delta H^{\ddagger} = 42.1 \pm 0.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = -2.0 \pm 0.4$ e.u.)[18] leads to an extra stabilization energy of 6.3 ± 2.0 kcal mol^{-1}, or 5.3 ± 1.3 kcal mol^{-1}, respectively, values which are greater than that of 3.6 ± 0.2 kcal mol^{-1} found in this work. If an explanation for the lack of congruence does not lie in the experimental uncertainties, we can offer no other.[19]

Conclusions

The results of an attempt to evaluate the dependence of conjugative interaction in styrenes on dihedral angle in the direction of coplanarity[1] is suggestive of a small increase in stabilization energy (∼−0.4 kcal mol^{-1}) in response to a decrease in angle from ∼35° (*cis*-**6**) to ∼21° (*cis*-**8**) (Chart 1). But reservations about the quantitative reliability of the conclusion remain owing to a lack of confidence in the ability of molecular mechanical estimations to correct for the steric component at an apposite level of thermochemical accuracy.

The effect of dihedral angle on stabilization energy in a cinnamyl radical is more secure. A similar decrease in dihedral angle, from 38° to 15°, between a benzene ring and an allyl radical leads to an increase in stabilization energy from −2.5 kcal mol^{-1} (**10**) to −3.6 kcal mol^{-1} (**9**), respectively, vis-à-vis allyl (**11**) (Scheme 3).

Experimental Section

General Procedures. ^1H and ^{13}C NMR (125.8 MHz) spectra are measured in the noted solvents by a Bruker AM-500 instrument (500 MHz). Spin−lattice relaxation times (T_1) are determined by the inversion−recovery method with use of vacuum-sealed solutions in toluene-d_8. Chemical shifts are reported in ppm (δ) with respect to TMS; coupling constants, *J*, are reported in hertz. Infrared spectra are measured on a Nicolet Impact 400D FT-IR instrument and reported in cm^{-1}. UV−vis spectra are measured on a Varian Cary 1 E UV−visible spectrophotometer and reported as λ_{max} in nm (extinction coefficients

(14) Doering, W. v. E.; Kitagawa, T. *J. Am. Chem. Soc*. **1991**, *113*, 4288−4297.

(15) The activation parameters reported in ref 10 for the equilbration of *anti*- and *syn*-**10** have been confirmed by repetition at 164.5 °C ($k_1 = 7.78 \pm 0.5\ s^{-6}$) and 184.3 °C ($k_1 = 45.8 \pm 0.9\ s^{-6}$): $E_a = 35.6$ kcal mol^{-1} and $\log A = 12.7$; $\Delta H^{\ddagger} = 34.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -3.3$ e.u.

(16) Ellison, G. B.; Davico, G. E.; Bierbaum, V. M.; DePuy, C. H. *Int. J. Mass Spectrosc. Ion Proc.* **1996**, *156*, 109−131.

(17) Doering, W. von E.; Beasley, G. H. *Tetrahedron* **1973**, *29*, 2231−2243.

(18) Orchard, S. W.; Thrush, B. A. *J. Chem. Soc. Chem. Commun.* **1973**, 14.

(19) Persistent concern about a possible difference between gas-phase and liquid-phase remains unresolved.

as log ϵ). Optical rotations are measured on a Perkin-Elmer Polarimeter 241. Enantiomeric excess (ee) is determined on a Hewlett-Packard 5890 Series 11 gas chromatograph with a Chiraldex GTA column: 20 m × 0.25 mm i.d. × 0.125 mm film, Advanced Separation Technology, Inc. High-resolution mass spectra (HR-MS) are measured on a JEOL AX 505 spectrometer equipped with a data-recovery system.

2-Methyl-1,2,3,4-tetrahydro-(2*H*)-naphthalen-1-one (1). This compound was prepared by a procedure modified from that of Cainelli et al.[2] by Rae and Umbrasas.[20] A mixture of iron pentacarbonyl (52.0 mL, 0.396 mol), potassium hydroxide (66.6 g, 1.19 mol), and ethanol (500 mL) was stirred and heated at reflux for 2 h. A solution of 1,2,3,4-dihydro-(2*H*)-naphthalen-1-one (α-tetralone, 38.4 g, 0.263 mol) and 37.2% aqueous formaldehyde (22.0 mL) was then added. The resulting mixture was boiled under reflux for 20 h, poured into water, and extracted with hexane. The hexane extract was washed with water and dried over anhydrous Na_2SO_4. Two distillations of the extract gave 24.4 g (58%) of colorless liquid: bp 122−125 °C (10 Torr) [lit.[3] 134−138 °C (16 Torr)]; ^{1}H NMR ($CDCl_3$) 8.04 (d, 1H, J = 7.6), 7.45 (t, 1H, J = 7.5), 7.30 (t, 1H, J = 7.5), 7.23 (d, 1H, J = 7.7), 3.05 (ddd, 1 H, J = 4.4, 11.1, 16.8), 2.97 (dt, 1H, J = 4.4, 16.7), 2.59 (m, 1H), 2.20 (dq, 1H, J = 4.4, 13.2), 1.89 (ddd, 1H, J = 4.7, 12.1, 24.3), 1.27 (d, 3H, J = 6.7); IR 2963, 2931, 2860, 1685, 1602, 1455, 1433, 1374, 1358, 1323, 1267, 1228, 968, 907, 739.

(±)-10a-Methyl-1,9,10,10a-tetrahydro-(2*H*)-phenanthren-3-one (3). This compound was prepared by the method reported by DeBoer.[3] A stream of nitrogen saturated with methyl vinyl ketone was bubbled through a solution of 2-methyl-1,2,3,4-tetrahydro-(2*H*)-naphthalen-1-one (**1**) (5.0 g, 31.2 mmol) and 1 mL of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in 15 mL of benzene. The reaction was monitored by gas chromatography until >96% of **1** had reacted (ca. 2 h). The mixture was diluted with 1% HCl and extracted with CH_2Cl_2. The organic layer was washed with $NaHCO_3$, dried over anhydrous Na_2SO_4, and concentrated. Purification by flash chromatography (silica gel, elution with hexane/ethyl acetate 6:1) afforded 5.5 g of Michael adduct **2**: ^{1}H NMR ($CDCl_3$) 8.02 (d, 1H, J = 7.7), 7.46 (t, 1H, J = 7.5), 7.30 (t, 1H, J = 7.5), 7.22 (d, 1H, J = 7.7), 3.01 (m, 1H), 2.51 (ddd, 1H, J = 5.7, 10.4, 17.4), 2.41 (ddd, 1H, J = 5.7, 10.2, 17.4), 2.13 (s, 3H), 2.08 (ddd, 1H, J = 5.2, 7.2, 13.6), 1.91 (m, 1H), 1.19 (s, 3H); IR 2962, 2929, 2857, 1715, 1679, 1600, 1454, 1355, 1223, 743.

Compound **2** was cyclized by boiling under reflux with 100 mL of 2% NaOH in 100 mL of 50:50 water/methanol for 2 h. The cooled mixture (0 °C) was neutralized with $NaHCO_3$. An extract with CH_2Cl_2 (3 × 60 mL) was washed with saturated NaCl (30 mL), dried (Na_2SO_4), and passed through a silica gel column (elution with hexane/ethyl acetate, 4:1). Removal of solvent in vacuo gave 4.3 g of (±)-**3** as a slightly yellow oil (65% overall): ^{1}H NMR ($CDCl_3$) 7.70 (d, 1H, J = 8.0), 7.33 (t, 1H, J = 7.4), 7.25 (t, 1H, J = 7.8), 7.20 (d, 1H, J = 7.6), 6.51 (s, 1H), 3.09 (m, 1H), 2.89 (dt, 1H, J = 3.7, 17.5), 2.67 (ddd, 1H, J = 5.7, 14.6, 17.4), 2.47 (ddd, 1H, J = 2.3, 4.6, 17.4), 1.98 (ddd, 1H, J = 4.6, 13.4, 14.5), 1.91 (ddd, 1H, J = 2.3, 4.6, 13.4), 1.80 (m, 2H), 1.21 (s, 3H); IR 2964, 2923, 2853, 1662, 1588, 1449, 1455, 1345, 1325, 1277, 1249, 1234, 1209, 782, 768.

Resolution of (±)-**3** was effected by HPLC on a Chiralcel OJ semipreparative column (hexane/isopropyl alcohol, 95:5). The first compound to separate was (10a*R*)-(−)-10a-methyl-1,9,10,10a-tetrahydro-(2*H*)-phenanthren-3-one, (10a*R*)-(−)-**3**: 100% ee, $[\alpha]^{20}_{589}$ −406°; $[\alpha]^{20}_{578}$ −432° (*c* 3.09, ethanol) (lit.[21] $[\alpha]_{589}$ −436°, $CHCl_3$). The second was (10a*S*)-(+)-**3**: 100% ee, $[\alpha]^{20}_{589}$ +408°; $[\alpha]^{20}_{578}$ +433° (*c* 3.12, ethanol) (lit.[21] $[\alpha]_{589}$ +440°, $CHCl_3$; (lit.[22] $[\alpha]^{25}_{578}$ +428°, $CHCl_3$).

10a,10a′-Dimethyl-1,1′,9,9′,10,10′,10a,10a′-octahydro-3,3′-bi-(2*H*)-phenanthrylidene (9). This compound was prepared by the reaction of McMurry−Mukaiyama−Tyrlik closely following a published procedure,[13] in which $TiCl_4$ (3.0 mL, 5.2 g, 27 mmol) was added with a syringe to cooled (0 °C, ice water), freshly distilled THF (30 mL) under nitrogen followed by activated Zn dust (3.5 g, 54 mmol) in portions. After 10 min of stirring, 1 mL of dry pyridine was added by syringe. The resulting mixture was stirred for an additional 10 min. A solution of (10a*S*)-(+)-**3** (0.51 g, 2.4 mmol) in THF (10 mL) was added dropwise, the reaction being continued at 0 °C for 1 h. The mixture was diluted with 30 mL of pentane and 30 mL of ethyl ether and then filtered through Celite. The organic layer was washed with aqueous NH_4Cl (2 × 20 mL), brine (2 × 20 mL), and dried over Na_2SO_4. Removal of the solvent afforded, after flash chromatography on silica gel (hexane), 0.49 g of a yellow oil, recrystallization of which from 1 mL of pentane gave 250 mg of (*S,S*)-(+)-*anti*-**9**. A second recrystallization from ethyl acetate afforded 98 mg (42%) of yellow needles: mp 209−210 °C; $[\alpha]^{20}_{589}$ +86° (*c* 1.12, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 7.80 (d, 2H, J = 7.3), 7.30 (s, 2H), 7.14−6.97 (m, 6H), 2.90 (ddd, 2H, J = 6.1, 12.3, 17.1), 2.83 (dt, 2H, J = 3.3, 14.7), 2.62 (ddd, 2H, J = 2.2, 5.0, 17.0), 2.48−2.40 (m, 2H), 1.65−1.48 (m, 8H), 1.00 (s, 6H); ^{13}C NMR ($CDCl_3$) 141.31, 136.24, 135.15, 130.95, 129.75, 127.21, 126.40, 124.70, 119.54, 38.62, 37.89, 33.52, 26.60, 22.49, 21.88; IR 2958, 2916, 2846, 1482, 1468, 1453, 1380, 1268, 1186, 1106, 885, 769, 758, 724; UV−vis 383 (4.780), 199 (4.719); HR-MS calcd for $C_{30}H_{32}$ 392.2504, found 392.2494.

Concentration of the mother liquor to ca. 0.5 mL and storing at 10 °C overnight yielded 110 mg of a more soluble, crystalline product. Recrystallization from pentane afforded 81 mg of (*S,S*)-(−)-*syn*-**9** (17%) as yellow crystals: mp 162−164 °C; $[\alpha]^{20}_{589}$ −4.4° (*c* 1.08, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 7.70 (d, 2H, J = 7.6), 7.66 (s, 2H), 7.03−6.95 (m, 6H), 2.88 (ddd, 2H, J = 6.0, 12.7, 17.0), 2.62 (ddd, 2H, J = 2.0, 5.3, 17.1), 2.54 (ddd, 2H, J = 2.9, 4.4, 15.8), 2.44 (dt, 2H, J = 4.7, 14.9), 1.63−1.50 (m, 8H), 1.00 (s, 6H); ^{13}C NMR ($CDCl_3$) 140.66, 136.12, 135.12, 131.36, 129.59, 127.16, 126.58, 124.73, 117.97, 38.69, 38.07, 33.55, 26.63, 23.92, 21.83; IR 2958, 2916, 2846, 1482, 1468, 1453, 1380, 1268, 1186, 1106, 885, 769, 758, 724; UV−vis: 379 (4.732), 199 (4.712); HR-MS calcd for $C_{30}H_{32}$ 392.2504, found 392.2513.

Distinction between *anti*-**9** and *syn*-**9** relied on nuclear Overhauser enhancement: irradiation at 7.30 ppm (H-4 of *anti*-**9**) showed an enhancement at 2.83 ppm (H-2 of *anti*-**9**) of 12%, while irradiation at 7.66 ppm (H-4 of *syn*-**9**) showed no enhancement at 2.62 ppm (H-2 of *syn*-**9**).

Kinetics of the Anti−Syn Isomerization of (*S,S*)-10a,10a′-Dimethyl-1,1′,9,9′,10,10′,10a,10a′-octahydro-3,3′-bis-(2*H*)-phenanthrylidene (9). A solution of 5.0 mg of crystalline (*S,S*)−(+)-*anti*-**9** and ca. 5% mol 18-crown-6 ether as internal standard in 0.5 mL of toluene-d_8 in an NMR tube (treated with 10% aqueous KOH for 20 h and washed with distilled water, and analytical grade acetone) was degassed by three freeze−pump−thaw cycles and sealed under vacuum (10^{-5} Torr). An NMR reading at zero time was taken, and the sealed NMR tube was heated in a constant temperature vapor bath for the designated periods of time.

The temperature of the heating bath was measured with a J-type thermocouple connected to a Leeds and Northrup Model 8686 millivolt potentiometer using ice−water as a reference junction. Temperature was recorded immediately before and immediately after each heating period. However, during longer runs, temperature was recorded every 12−18 h without disturbing the kinetic experiment. The temperature of each heating period was taken as the mean of the temperature recorded before and after the kinetic run. The mean of the temperatures of the individual intervals was considered the average temperature of the kinetic experiment.

The boiling solvents used as the constant temperature vapor bath (a convenient method which suffers from variations in atmospheric pressure) in the various kinetic experiments were as follows: *o*-xylene (143.9−145.5 °C), cumene (151.7−152.7 °C), mesitylene (164.4−164.9 °C), *p*-cymene (176.5−177.2 °C), and diethyl oxalate (184.2−184.5 °C).

Quantitative ^{1}H NMR spectra were measured allowing an interpulse time-delay (relaxation delay and saturation period) of at least five times the longest spin lattice relaxation time of the concerned protons. NMR analysis (500 MHz) was effected by using the H-4 signals at 7.30 ppm of *anti*-**9** and 7.66 ppm of *syn*-**9**. Recovery was determined from the ratio of the sums of the areas of the H-4 peaks [7.30 ppm (*anti*-**9**) and 7.66 ppm (*syn*-**9**)] and the H-5 peaks [7.30 ppm (*anti*-**9**) and 7.66 ppm (*syn*-**9**)] to the area of the internal standard, 18-crown-6 (3.50 ppm). Results are given in Tables 1 and 2. Reaction rates and equilibrium constants at each of the individual temperatures were optimized

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simultaneously by the nonlinear least-squares method to fit the reversible first-order kinetic equation to the observed data. The activation parameters were calculated from the observed rate and equilibrium constants at the various temperatures.

1,2,3,4,4aα,9,10,10a-Octahydro-10a*β*-methylphenanthrene-3-ol (4). Three grams of Pd/C (1%) was added under argon to a stirred solution of 10 g (47.1 mmol) of **3** in 30 mL of ethanol in a hydrogenation bomb. After being sealed, the bomb was freed of remaining air/argon by charging and releasing five times with hydrogen (20 bar). Finally, the mixture was stirred for 18 h at room temperature under 20 bar of hydrogen. The black suspension was filtered and washed thoroughly with 250 mL of ethanol. Solvent was removed; 100 mL of hexanes was added to the light yellowish oil, and the cloudy liquid was filtered and concentrated in vacuo. Dissolving in 60 mL of hexanes and crystallization at 0 °C afforded 9.0 g (41.6 mmol, 88%) of a mixture of diastereomers of **4**. Recrystallization of the colorless crystals at room temperature from hexanes/ethyl acetate (slow evaporation of solvent) yielded 6.6 g (30.6 mmol, 65%) of colorless needles of the major isomer: mp 112 °C; R_f (hexane/ethyl acetate 5:1) 0.15; ^{1}H NMR (C_6D_6) 7.20−6.95 (m, 4H), 3.44 (m, 1H), 2.75 (m, 1H), 2.62 (m, 1H), 2.34 (dm, 1H), 2.20 (dd, 1H), 1.71 (dm, 1H), 1.46 (m, 1H), 1.35−1.15 (m, 5H), 1.00 (td, 1H), 0.61 (s, 3H); ^{13}C NMR (C_6D_6) 139.77, 136.69, 129.48, 129.02, 126.50, 126.40, 125.53, 72.16, 44.52, 39.65, 38.78, 34.83, 32.76; IR (KBr) 3381, 2934, 2908, 1492, 1050; UV (hexanes) 268 (2.662), 214 (3.948), 202 (4.237); HR-MS calcd for $C_{15}H_{20}O$ 216.1514, found 216.1507; MS (70 eV) 216 (100), 198 (21), 157 (40), 129 (36), 115 (33).

1,4,4aα,9,10,10a-Hexahydro-10a*β*-methylphenanthren-3-one (*trans*-5). A solution of 6.9 g of CrO_3 in 13 mL of H_2O was mixed with 6 mL of concentrated sulfuric acid.[23] Addition of 1.5 mL of water provided a bright orange solution, of which 7.5 mL was added slowly to a stirred solution of 4.5 g (20.8 mmol) of *trans*-**4**, mp 112 °C, in 60 mL of acetone cooled to 0 °C. After completion of the addition, stirring was continued 1 h at 0 °C and 2 h at room temperature. The strongly acidic, blue suspension was poured into 300 mL of saturated aqueous $NaHCO_3$. Extraction of the resulting mixture with ethyl ether (3 × 100 mL) afforded a yellow organic layer, which was washed with brine (2 × 100 mL) and dried over anhydrous sodium sulfate. Filtration and concentration in vacuo afforded a yellow oil, which was crystallized by the addition of hexanes to provide 3.8 g (17.6 mmol, 85%) of colorless *trans*-**5**: mp 72 °C; R_f (hexane/ethyl acetate 5:1) 0.45; ^{1}H NMR (C_6D_6) 7.10−6.70 (m, 4H), 2.91 (m, 1H), 2.67 (m, 1H), 2.51 (m, 1H), 2.40 (dd, 1H), 2.20 (m, 1H), 2.10 (dd, 1H), 1.98 (t, 1H), 1.35−1.00 (m, 4H), 0.51 (s, 3H); ^{13}C NMR (C_6D_6) 208.63, 138.09, 135.58, 129.07, 126.27, 126.23, 125.13, 44.68, 41.10, 39.11, 37.66, 37.16, 31.86, 26.34, 14.66; IR(KBr) 2918, 1709, 1490; UV(hexanes) 266 (2.571), 256 (2.528), 214 (3.931), 202 (4.106); HR-MS calcd for $C_{15}H_{18}O$ 214.1358, found 214.1359; MS (70 ev) 214 (100), 181 (35), 144 (50), 129 (40), 115 (38).

Starting with the mixture of both isomers of **4** led to an 88:12 mixture of *trans*-**5** and *cis*-**5**. Recrystallization (hexanes/ethyl acetate 5:1 at 0 °C) enriched the trans isomer in the mother liquor and concentrated the cis isomer in the crystalline material. Therefore, pure *trans*-**5** can only be obtained from the mother liquors after complete removal of cis-**5**.

1,2,3α,9,10,10a-Hexahydro-10a*β*-methylphenanthren-3-ol and 1,2,3*β*,9,10,10a-Hexahydro-10a*β*-methylphenanthren-3-ol. A solution of 0.4 g (10.6 mmol) of $NaBH_4$ in 2 mL of methanol was added to a stirred solution of **3** (2.0 g, 9.4 mmol) in 15 mL of methanol. The yellow solution warmed to 40−45 °C, became colorless within a few minutes, and was stirred for an additional 30 min at room temperature. After addition of 50 mL of water and extraction with ethyl ether (3 × 50 mL), the combined organic solutions were washed with 50 mL of saturated brine, filtered, and concentrated in vacuo to a slightly yellow oil. Chromatography on 20 g of silica (cyclohexane/ethyl acetate 5:1) afforded 1.7 g (7.9 mmol, 84%) of an 88:12 mixture of carbinols as a colorless oil. Recrystallization from hexane/ethyl acetate provided 1.1 g (5.1 mmol, 54%) of the major isomer as colorless crystals: mp 127 °C; R_f (hexane/ethyl acetate, 5:1) 0.2; ^{1}H NMR (C_6D_6) 7.59 (dd, 1H), 7.03 (m, 2H), 6.94 (d, 1H), 6.15 (s, 1H), 4.20 (m, 1H), 2.76 (dq, 1H), 2.53 (dd, 1H), 1.86−1.81 (m, 2H), 1.59−1.51 (m, 1H), 1.43−1.32 (m, 3H), 1.23 (dt, 1H), 0.90 (s, 3H); ^{13}C NMR (C_6D_6) 142.48, 136.26, 135.05, 129.84, 127.97, 126.82, 126.01, 125.64, 68.93, 38.63, 37.52, 33.70, 29.48, 26.72, 22.93; IR(KBr) 3410, 2964, 2935, 1455, 1052; UV (hexanes) 294 (3.089), 286 (3.217), 256 (4.129), 216 (4.239); HR-MS calcd for $C_{15}H_{18}O$ 214.1358, found 214.1359; MS (70 eV) 214 (100), 196 (33), 181 (70), 157 (35), 144 (50). Minor isomer: ^{1}H NMR (C_6D_6) 7.49 (dd, 1H), 7.08 (m, 2H), 6.96 (d, 1H), 6.06 (d, 1H, J = 4.9), 4.12 (s, 1H), 2.77 (dq, 1H), 2.57 (dd, 1H), 1.74−1.70 (m, 2H), 1.70−1.61 (m, 1H), 1.52−1.41 (m, 2H), 1.28 (dt, 1H), 1.09 (s, 1H), 0.83 (s, 3H); ^{13}C NMR (C_6D_6) 136.77, 128.78, 128.60, 128.40, 128.26, 126.76, 125.90, 122.60, 65.48, 38.09, 34.06, 33.80, 28.29, 26.55, 21.74.

1,9,10,10a-Tetrahydro-10a-methylphenanthrene. Commercial grade $SOCl_2$ (0.7 mL, 9.5 mmol) was added under argon within 5 min to a stirred solution of anhydrous pyridine (0.8 g, 10.1 mmol) in 1 mL of $CHCl_3$ cooled in an ice/water bath. The pyridine/$SOCl_2$ complex was added under argon slowly with a syringe to a stirred solution of 1.7 g (7.9 mmol) of the mixture of carbinols above at −10 to −5 °C in an ice/NaCl/water bath. The yellow solution was stirred 30 min, diluted with 50 mL of cold $CHCl_3$, washed with cold saturated brine (3 × 50 mL), filtered, and concentrated in vacuo (bath 20 °C). The residual yellow oil was dissolved in 2 mL of cyclohexane and purified by chromatography on 20 g of silica gel (cyclohexane as eluent): first fraction, 0.5 g (2.6 mmol, 33%) of diene as a slightly yellow oil; second fraction (cyclohexane/ethyl acetate 10:1 as eluent), 0.7 g of an intensely yellow, unidentified solid; third fraction (cyclohexane/ethyl acetate 5:1 as eluent), 0.18 g (0.8 mmol, 11%) of the reverse isomer of the starting carbinol. The diene was further purified by vacuum distillation: R_f (cyclohexane/ethyl acetate 5:1) 0.75; ^{1}H NMR (C_6D_6) 7.65 (dd, 1H), 7.03 (m, 2H), 6.95 (d, 1H), 6.46 (d, 1H, J = 5.6), 6.01 (m, 1H, J = 9.4), 5.68 (dq, 1H), 2.82 (dq, 1H), 2.48 (dq, 1H), 2.23 (dt, 1H), 1.88 (dd, 1H), 1.53 (dt, 1H), 1.42 (dq, 1H), 1.00 (s, 3H); ^{13}C NMR (C_6D_6) 140.03, 137.03, 133.71, 130.24, 127.67, 126.91, 125.88, 125.68, 124.47, 116.25, 40.32, 37.67, 33.92, 27.39, 21.13; IR(film) 3036, 2919, 2851, 1560, 1485; UV (hexanes) 326 (4.068), 312 (4.035), 248 (3.773), 242 (3.849), 204 (4.209); GC-MS 196 (70), 181 (100), 165 (60).

1,4,4aα,9,10,10a-Hexahydro-10a*β*-methyl-3-phenylphenanthrene (*trans*-7). A 3 M solution of phenylmagnesium bromide (8 mL, 24 mmol) in ether was added over a 30-min period to a solution of 3.29 g (15.4 mmol) of ketone, *trans*-**5**, mp 72 °C, in 65 mL of anhydrous THF at 0 °C. The mixture was stirred for 2 h at 0 °C and 3 h at room temperature, quenched with 100 mL of aqueous NH_4Cl, and extracted with ether (3 × 100 mL). The combined organic layers were washed with 100 mL of brine, filtered, and concentrated in vacuo to provide a slightly yellow oil, which was mixed with 200 mL of toluene and 0.8 g of *p*-toluenesulfonic acid. After the solution was boiled under reflux for 2 h and the evolved water was separated, the cooled, reddish brown solution was poured into 100 mL of $NaHCO_3$ and extracted with hexanes (2 × 100 mL). The combined organic layers were washed with 150 mL of brine, dried over potassium carbonate, filtered, and concentrated in vacuo. The yellow oil was diluted with 1 mL of hexanes and purified by chromatography on 50 g of silica gel with hexanes as the eluent. Removal of the solvent left 3.7 g (13.5 mmol, 86%) of a 96:4 colorless mixture of phenylphenanthrenes *trans*-**7** and *trans*-**6**, crystallization of which from hexanes yielded 3.3 g (12.0 mmol, 78%) of pure *trans*-**7**: mp 116 °C; ^{1}H NMR (C_6D_6) 7.40 (d, 2H), 7.23 (m, 3H), 7.13 (m, 4H), 7.03 (m, 1H), 6.00 (m, 1H), 2.99 (dd, 1H, J = 16.8, 4.8), 2.82 (m, 1H, J = 17.0, 12.1, 6.5), 2.66 (m, 1H, J = 11.6, 5.3), 2.58 (m, 1H, J = 17.1, 5.3), 2.31 (m, 1H, J = 14.6, 13.9, 2.0), 1.92 (dm, 1H), 1.90 (dm, 1H, J = 17.6, 5.3, 2.0), 1.41 (dm, 1H, J = 13.8, 6.5, 1.8), 1.41 (td, 1H, J = 12.7, 12.7, 6.0), 0.76 (s, 3H); ^{13}C NMR (C_6D_6) 142.71, 139.28, 136.35, 136.22, 129.24, 128.53, 128.30, 127.92, 126.99, 126.46, 126.25, 125.95, 125.57, 123.36, 42.10, 41.86, 37.42, 30.79, 29.96, 26.52, 16.35; IR(KBr) 3081−2820, 1650, 1599, 1492, 749, 692; UV (hexanes) 248 (4.072), 214 (4.219); HR-MS calcd for $C_{21}H_{22}$ 274.1722, found 274.1721; GC-MS 274 (100), 259 (15), 157 (60), 144 (37), 129 (45).

For X-ray crystallographic analysis, a single crystal was grown from hexanes at 0 °C.

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1,2,3a,9,10,10a-Hexahydro-10a*β*-methyl-3-phenylphenanthrene (*cis*-8). A solution of 0.9 g (3.28 mmol) of *trans*-**7** in 2 mL of cyclohexane was added to 80 mL (8 mmol) of a 0.1 M solution of potassium *tert*-butoxide in HMPT. The solution became dark violet instantly. After being stirred under argon for 2 days at 55−60 °C, the solution was quenched with 50 mL of water, treated with 50 mL of brine, and extracted with hexanes (3 × 100 mL). The combined organic layers were washed with 100 mL of brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The remaining yellow oil was purified on 40 g of silica gel, hexanes as eluent, to provide 0.85 mg (3.1 mmol, 95%) of a colorless oil consisting mainly of *cis*-**8**, which could be crystallized from pentane at 0 °C to yield 0.71 g (2.59 mmol, 79%) of a single isomer: mp 113 °C; ^{1}H NMR (C_6D_6) 7.44 (d, 1H), 7.21 (m, 4H), 7.14 (m, 1H), 7.06 (td, 1H), 7.00 (t, 2H), 6.14 (d, 1H, J = 2.0), 3.39 (m, 1H, J = 6.0, 11.0), 2.85 (m, 1H, J = 16.6, 12.8, 6.0), 2.61 (dd, 1H, J = 5.0), 1.85 (m, 1H), 1.71 (m, 1H), 1.49 (m, 4H), 1.01 (s, 3H); ^{13}C NMR (C_6D_6) 147.11, 141.27, 135.42, 135.04, 129.36, 128.88, 128.29, 127.93, 127.44, 127.13, 126.50, 126.30, 125.36, 124.72, 44.76, 39.19, 38.22, 32.95, 29.34, 26.28, 23.05; IR (KBr) 3072−2866, 1634, 1600, 1488, 755, 703; UV (hexanes) 256 (4.273), 214 (4.387); HR-MS calcd for $C_{21}H_{22}$ 275.1800, found 275.1799; GC-MS 275 (100), 259 (2), 183 (1), 157 (4).

For X-ray crystallographic analysis, a single crystal was grown from a dilute solution in ethanol by slow evaporation at room temperature.

Note that any mixture of the isomers of the phenylphenanthrenes can be converted to *cis*-**8** by this procedure followed by crystallization as described above.

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Supporting Information Available: Plot of the equilibrium data among *cis*-**8**, *cis*-**6**, *trans*-**8**, and *trans*-**6** over the temperature range 61−178 °C, kinetic data of the thermal equilibration of *syn*- and *anti*-**10** at 164.5 and 184.3 °C in benzene-d_6, and kinetic data of the equilibration of *syn*- and *anti*-**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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