

Conjugative Interaction in Styrenes

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Abstract: Conjugative interactions of the carbon–carbon double bond are fundamental in organic chemistry. In this work, equilibria are established among conjugated and unconjugated isomers of two β -substituted styrenes, 1-phenylbut-1-ene and 1-phenyl-3-methylbut-1-ene, and one α,β -disubstituted styrene, 2-phenyl-5-methylhex-2-ene, over a range of temperatures (the van't Hoff method) in hexamethylphosphoric triamide and potassium *tert*-butoxide. From the *trans* styrenes of the first two sets, an enthalpy of conjugative interaction of phenyl *vis-à-vis* alkyl ($\Delta\Delta H_{\text{ConjInter/Alk}} = -2.5 \pm 0.2$ kcal/mol [-5.1 kcal/mol defined as phenyl *vis-à-vis* hydrogen ($\Delta\Delta H_{\text{ConjInter/H}} = -2.7$ kcal/mol). The *cis* styrenes reveal an attenuated $\Delta\Delta H_{\text{ConjInter/Alk}}$ of -1.1 kcal/mol ($\Delta\Delta H_{\text{ConjInter/H}} = -2.7$ kcal/mol). The α -methyl group in the third set also leads to a reduced conjugative interaction. Entropy plays an important role in determining positions of equilibrium. Free energies of conjugation are reported for several sterically hindered *o*-methyl-substituted styrenes.

Background to Conjugative Interaction

Thermochemical consequences of the interaction of a wide variety of substituents with the carbon–carbon double bond have a long history in organic chemistry. The subject has been exhaustively reviewed by Hine and his co-workers.⁴ Thermochemical information about styrenes being sparse, this paper is focused on the enthalpy and entropy of conjugation of the phenyl group and the influence of substituents and configuration on deviations from coplanarity.

Analysis of thermochemical data in the literature^{5,6} relevant to styrene affords various estimates of the enthalpy of conjugative interaction. From heats of formation (gas) of styrene (\mathbf{a}_0) and ethylbenzene (\mathbf{a}_2) compared to vinylcyclohexane (\mathbf{m}_0) and ethylcyclohexane (\mathbf{m}_2), an enthalpy of conjugation of phenyl with ethene relative to that of alkyl with the carbon–carbon double bond may be obtained.⁷ A value may also be derived from the heat of hydrogenation of *trans*-stilbene (\mathbf{b}_0) to bibenzyl (\mathbf{b}_2) by comparison with the mean of those of *trans*-1,2-dialkylethenes (*vide infra*).^{8,9} Bearing on conjugative interaction in α -substituted styrenes are heats of hydrogenation of 2,5-diphenylhexa-1,5-diene and 2,6-diphenylhepta-1,6-diene.^{10,11} These analyses bring to light substantial ambiguity in the selection of a trustworthy value for the enthalpy of conjugation of phenyl *vis-à-vis* alkyl: somewhere between -0.6 and -3.3 kcal/mol seems credible.^{7,8,11–13}

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(5) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.

(6) Rogers, D. W.; McLafferty, F. J. *Tetrahedron* **1971**, 21, 3765–3775.

The great majority of conjugative interactions has been obtained by the measurement of equilibrium constants in the

(7) For \mathbf{a}_0 (PNK,⁵ p 267), values of $\Delta_f H^\circ(\text{liq})$, +24.73 and +24.91 kcal/mol (mean, 24.82 kcal/mol), and of ΔH_{vap} , +10.50 and +9.47 kcal/mol, are given, from which $\Delta_f H^\circ(\mathbf{a}_0, \text{gas})$ range from +35.32 to +34.29 kcal/mol. For \mathbf{a}_2 (p 268), $\Delta_f H^\circ(\text{liq})$ are -2.95 and -3.55 kcal/mol and ΔH_{vap} is +10.10 kcal/mol, from which $\Delta_f H^\circ(\mathbf{a}_2, \text{gas})$ are +7.15 and +6.55 kcal/mol, respectively. From these combustion data, values for $\Delta_f H_{\text{H}_2}(\mathbf{a}_0 \rightarrow \mathbf{a}_2, \text{gas})$ range from -27.14 to -28.77 kcal/mol. For \mathbf{m}_0 (p 270), $\Delta_f H^\circ(\text{liq})$, -21.19 kcal/mol, and ΔH_{vap} , +9.50 kcal/mol, give $\Delta_f H^\circ(\mathbf{m}_0, \text{gas})$, -11.69 kcal/mol. For \mathbf{m}_2 (p 273), $\Delta_f H^\circ(\text{liq})$, -50.70 kcal/mol, and ΔH_{vap} , +9.57 and +9.67 kcal/mol (mean, +9.62 kcal/mol), lead to $\Delta_f H^\circ(\mathbf{m}_2, \text{gas})$, -41.08 kcal/mol. From these data, a value for $\Delta_f H_{\text{H}_2}(\mathbf{m}_0 \rightarrow \mathbf{m}_2, \text{gas})$ of -29.39 kcal/mol is derived. Values for the enthalpy of conjugation of styrene between -0.62 and -2.25 kcal/mol are acceptable. If the lower value for $\Delta H_{\text{vap}}(\mathbf{a}_0)$ (+9.47 kcal/mol) is ignored and mean values for $\Delta_f H^\circ(\mathbf{a}_0, \text{gas})$ and $\Delta_f H^\circ(\mathbf{a}_2, \text{gas})$ of +35.32 and +6.85 kcal/mol, respectively, is taken, $\Delta_f H_{\text{H}_2}(\mathbf{a}_0 \rightarrow \mathbf{a}_2, \text{gas})$ of -28.47 kcal/mol is derived and a value for $\Delta H_{\text{conj}}(\mathbf{a}_0)$ of -0.92 kcal/mol results. Experimental values for heats of hydrogenation (gas) of \mathbf{a}_0 and \mathbf{a}_2 to \mathbf{m}_2 (-76.50 and -48.18 kcal/mol, respectively) lead to $\Delta_f H_{\text{H}_2}(\mathbf{a}_0 \rightarrow \mathbf{a}_2, \text{gas})$ of -28.32 kcal/mol and $\Delta H_{\text{conj}}(\mathbf{a}_0)$ of -1.07 kcal/mol. An experimental determination of $\Delta_f H_{\text{H}_2}(\mathbf{m}_0 \rightarrow \mathbf{m}_2, \text{liq})$ of -27.90 kcal/mol leads to a positive value for $\Delta H_{\text{conj}}(\mathbf{a}_0)$ of +0.42 kcal/mol.⁸

(8) Williams, R. B. *J. Am. Chem. Soc.* **1942**, 64, 1395–1404.

(9) From two values for $\Delta_f H^\circ(\mathbf{b}_0, \text{solid})$, +32.72 and +33.58 kcal/mol (PNK,⁵ p 304), and one for ΔH_{sublim} , +23.71 kcal/mol, two values for $\Delta_f H^\circ(\mathbf{b}_0, \text{gas})$, +56.43 and +57.29 kcal/mol, are derived; from two values for bibenzyl (\mathbf{b}_2) (p 305), $\Delta_f H^\circ(\mathbf{b}_2, \text{solid})$, +11.87 and +12.32 kcal/mol, and ΔH_{sublim} , +21.84 kcal/mol (a much lower value, +20.10 kcal/mol, is not taken), $\Delta_f H^\circ(\mathbf{b}_2, \text{gas})$, +33.71 and +34.16 kcal/mol, are derived; resulting $\Delta_f H_{\text{H}_2}(\mathbf{b}_0 \rightarrow \mathbf{b}_2, \text{gas})$ range from -22.27 to -23.58 kcal/mol. If a mean value for *trans*-1,2-dialkylethenes of -27.25 ± 0.05 kcal/mol (*vide infra*) is taken as the model, $\Delta H_{\text{conj}}(\mathbf{b}_0)$ of -3.67 to -4.98 kcal/mol or $\Delta H_{\text{conj}}(\mathbf{a}_0)$ of -1.84 to -2.49 kcal/mol results. Hydrogenation data,⁸ $\Delta_f H_{\text{H}_2}(\mathbf{b}_0 \rightarrow \mathbf{b}_2, \text{gas}) = -20.6$ kcal/mol, lead to $\Delta H_{\text{conj}}(\mathbf{b}_0)$ of -6.65 kcal/mol or $\Delta H_{\text{conj}}(\mathbf{a}_0)$ of -3.33 kcal/mol.

(10) Roth, W. R.; Lennartz, H.-W.; Doering, W. v. E.; Birladeanu, L.; Guyton, C. A.; Kitagawa, T. *J. Am. Chem. Soc.* **1990**, 112, 1722–1732.

(11) 2,5-Diphenylhexa-1,5-diene ($\Delta_f H_{\text{H}_2}$, -56.65 kcal/mol) and 2,6-diphenylhepta-1,6-diene ($\Delta_f H_{\text{H}_2}$, -55.67 kcal/mol) (mean, -56.16 kcal/mol) may be compared with hexa-1,5-diene ($\Delta_f H_{\text{H}_2}$, -60.1 kcal/mol) and hepta-1,6-diene ($\Delta_f H_{\text{H}_2}$, -60.2) or twice that of 1-alkylethenes ($\Delta_f H_{\text{H}_2}$, -59.82), from which conjugative interaction per phenyl *vis-à-vis* hydrogen becomes -2.0 or -1.83 kcal/mol. These values are almost identical with that resulting from replacement of vinyl hydrogen by alkyl, -2.01 kcal/mol (cf. Figure 1), whence conjugative interaction in these examples might appear to be $+0.18 \pm 0.5$ kcal/mol.

(12) Compare Table 41 (p 1091) of ref 13, in which the value, -2.2 kcal/mol, is proposed.

system of α,β -conjugated and β,γ -unconjugated isomers at a single temperature and has therefore furnished *free energies* of conjugation. Theoretical scrutiny has had to be based on the assumption that free energies and enthalpies are equal for practical purposes, that is, that entropies of conjugation can be ignored.⁴ Evaluation of this assumption is but one justification for dissecting free energy of conjugation into its components. Another is the desirability of providing more accurate data against which the enthalpic results of quantum and molecular mechanical calculational methods may be tested more rigorously.

Given a cleanly catalytic system for establishing equilibrium constants over a wide range of temperature and an analytical method of sufficient accuracy, the van't Hoff method¹⁴ offers an attractive experimental approach. Sensitivity is greatest when $\ln K \sim 0$ and decreases as the absolute value of $\ln K$ increases. Accuracy is ultimately limited by the analytical method and usually begins to falter when $\ln K$ falls outside a range of ± 4 . A major advantage, as noted explicitly by Benson and Bose in their work on the butenes,¹⁵ lies in an accuracy in $\Delta\Delta H$ significantly higher than can be obtained in general from differences between two enthalpies of formation determined by combustion, hydrogenation, or other chemical transformations.

A major series of van't Hoff studies by Taskinen and co-workers has included an investigation of the phenylpropenes, which is relevant to styrene.¹⁶ Allylbenzene being the compound of reference, conjugative interaction is relative to hydrogen. Resulting values of $\Delta\Delta_f H$ and $\Delta\Delta_f S$ for *trans*-1-phenylpropene *vis-à-vis* 3-phenylpropene are -5.57 kcal/mol and -3.24 cal mol⁻¹ K⁻¹ (eu), respectively, but the method is stretched in this instance because $\ln K$ ranges between 4 and 7.

Steric factors need to be considered in the interaction of phenyl with the carbon-carbon double bond beyond that in styrene itself and *trans*- β -substituted styrenes, in which they are assumed to be negligible by definition. These factors are less important in butadienes, for example, where special constitutional perturbations are required to enforce a significant departure from coplanarity.¹⁷⁻¹⁹ But in styrenes, a *cis* orientation of β -substituents, the presence of substituents in the α -position or in the ortho positions of the phenyl ring, can be expected sterically to cause deviations from the coplanar conformation optimum for π -electron delocalization.

Enthalpies of Conjugative Interaction of Alkyl Ethenes

Because equilibria in simple allyl systems are frequently too one-sided to furnish much more than qualitative indications of relative conjugative ability, in this study phenyl is pitted against sterically innocuous, but significantly conjugating, alkyl groups to achieve more favorable equilibrium constants. The resulting enthalpies of conjugation of phenyl *vis-à-vis* alkyl, to be translated into enthalpies of conjugation *vis-à-vis* hydrogen, require correction for enthalpy of conjugation of the apposite alkyl groups.

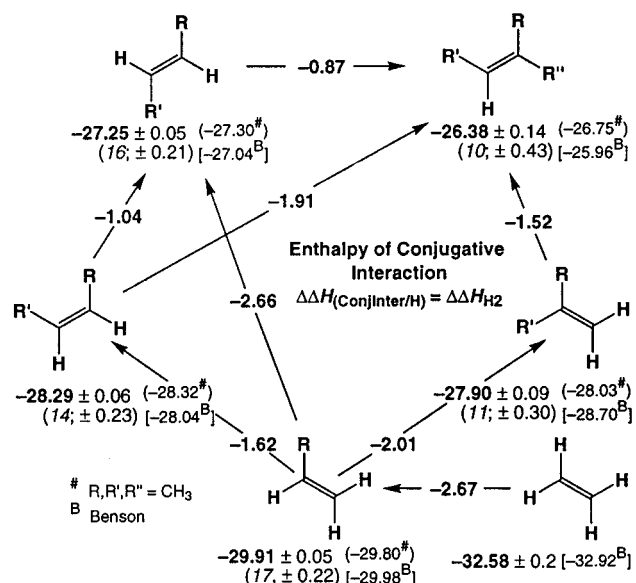


Figure 1. The various thermochemical data, available as Supporting Information,^{5,20,21} are translated into enthalpies of hydrogenation ($\Delta\Delta H_{H_2}$) and summarized as mean values (in kcal/mol) \pm the standard deviation of the mean, $s/n^{0.5}$. In parentheses, the *number* of examples, n , of each type and the sample standard deviation, s , are also given. Heats of hydrogenation of the simplest methyl-substituted examples are shown along side in parentheses. Also shown are values calculated by Benson's values for group equivalents.^{31c} Enthalpies of conjugative interaction, as each additional alkyl group is added, are synonymous with differences in heats of hydrogenation.

Values for conjugative interactions (thermochemical perturbations) of alkyl groups in mono-, di-, and trisubstituted olefins (five types) are estimated by an exhaustive examination of the data on enthalpies of hydrogenation from Rogers,²⁰ enthalpies of hydration from Wiberg,²¹ and heats of formation from Pedley, Naylor, and Kirby.^{5,22} Data are expressed in Figure 1 as *mean* values of enthalpies of hydrogenation (ΔH_{H_2}), while differences between heats of hydrogenation define the enthalpy of conjugative interaction of alkyl groups *vis-à-vis* hydrogen as a reference ($\Delta\Delta H_{\text{ConjInter/H}}$). Although no model can serve objectively as a *best* reference for comparison, the mean value of several compounds of the type appeals to us, because it has a standard deviation of the mean less than the experimental uncertainty associated with any single example that might be chosen, also arbitrarily, as a model.

In monosubstituted and *trans*-disubstituted ethenes, conjugative interaction of alkyl groups is -2.66 kcal/mol. However, in the other types of olefins, $\Delta\Delta H_{\text{ConjInter/H}}$ is not a constant, but decreases dramatically with substitution. Thus, in *cis*-disubstituted ethenes, it is only -1.62 kcal/mol, the difference of -1.04 kcal/mol being widely equated with an enthalpy of steric repulsion. Also worthy of note is a decrease in 1,1-disubstituted ethenes ($\Delta\Delta H_{\text{ConjInter/H}} = -2.01$ kcal/mol) of 0.65 kcal/mol, presumably stemming from a smaller but still significant steric interaction. The absence of this correction in the Benson scheme leads to the only large discrepancy between the generalized values in Figure 1 and the comparable Benson values [$\Delta\Delta H_{H_2}$ in brackets^B]. Trisubstituted ethenes, which

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(22) Data involving *tert*-butyl and similarly sterically crowded groups have been omitted, but their inclusion would not have influenced the outcome.

Chart 1

Series 1					
	1a(E)	1b(E)	1a(Z)	1b(Z)	
C ₆ D ₆ , RuH					
1	$\Delta\Delta G$ (298 °C)	-1.94	0.00	+0.55	+0.91
2	$\Delta\Delta_f H$ (kcal/mol)	-2.46±0.07	0.00	+0.28±0.25	+1.06±0.34
3	$\Delta\Delta_f S$ (cal mol ⁻¹ K ⁻¹)	-1.76±0.19	0.00	-0.92±0.69	+0.51±0.93
HMPT, RO ⁻					
4	$\Delta\Delta G$ (298 °C)	-2.08	0.00	+0.43	
5	$\Delta\Delta_f H$ (kcal/mol)	-2.80±0.11	0.00	-0.08±0.14	
6	$\Delta\Delta_f S$ (cal mol ⁻¹ K ⁻¹)	-2.42±0.35	0.00	-1.72±0.45	
7	$\Delta\Delta_f H_{\text{exp}}(\text{wtd mean})$	-2.55	0.00	+0.05	+1.06
8	$\Delta_f H^{\text{P}}_{\text{estimated}}$	+21.77	+24.32 ³²	+24.37	+25.38
9	$\Delta\Delta_f H^{\text{P}}_{\text{MMEVBH}}$	-1.47	0.00	+0.35	+1.34
10	$\Delta_f H^{\text{P}}_{\text{MMEVBH}}$	+21.90	+23.37	+23.72	+24.71
11	$\Delta\Delta_f H^{\text{P}}_{\text{MM3}}$	-1.13	0.00	+1.32	+0.92
12	$\Delta_f H^{\text{P}}_{\text{MM3}}$	+21.07	+22.20	+23.52	+23.12

Series 2					
	2a(E)	2b	2a(Z)	2c	
HMPT, RO ⁻					
1	$\Delta\Delta G$ (298 °C)	-0.54	0.00	+2.34	+1.38
2	$\Delta\Delta_f H$ (kcal/mol)	-1.57±0.05	0.00	+0.80±0.14	+1.36±0.10
3	$\Delta\Delta_f S$ (cal mol ⁻¹ K ⁻¹)	-3.42±0.15	0.00	-5.12±0.43	-0.04±0.31
4	$\Delta_f H^{\text{P}}_{\text{estimated}}$	+15.05 +15.21	+16.62 ³³ +16.78	+17.42 +17.58	+17.98 +18.49 ³³
5	$\Delta\Delta_f H^{\text{P}}_{\text{MMEVBH}}$	-0.41	0.00	+1.08	+0.53
6	$\Delta_f H^{\text{P}}_{\text{MMEVBH}}$	+15.24	+15.65	+16.73	+16.18
7	$\Delta\Delta_f H^{\text{P}}_{\text{MM3}}$	+0.10	0.00	+2.40	+3.43
8	$\Delta_f H^{\text{P}}_{\text{MM3}}$	+14.02	+13.92	+16.32	+17.35

Series 3						
	3a(E)	3b	3a(Z)	3c	3d	
HMPT, RO ⁻						
1	$\Delta\Delta G$ (298 °C)	-0.69	0.00	+0.43	+1.48	+1.58
2	$\Delta\Delta_f H$ (kcal/mol)	-1.08±0.05	0.00	0.00±0.08	+1.15±0.08	+1.58±0.10
3	$\Delta\Delta_f S$ (cal mol ⁻¹ K ⁻¹)	-1.27±0.11	0.00	-1.40±0.21	-1.10±0.21	-0.01±0.26
4	$\Delta_f H^{\text{P}}_{\text{estimated}}$	+4.43 +4.56	+5.51 ³⁴ +5.64	+5.51 +5.64	+6.66 +6.78	+7.09 +7.22 ³⁴
5	$\Delta\Delta_f H^{\text{P}}_{\text{MMEVBH}}$	-1.13	0.00	-0.51	+0.25	+0.78
6	$\Delta_f H^{\text{P}}_{\text{MMEVBH}}$	+1.94	+3.07	+2.56	+3.32	+3.85
7	$\Delta\Delta_f H^{\text{P}}_{\text{MM3}}$	-2.88	0.00	-2.78	-0.01	+2.16
8	$\Delta_f H^{\text{P}}_{\text{MM3}}$	+1.60	+4.48	+1.70	+4.47	+6.64

might be expected to have a $\Delta\Delta H_{\text{ConjInter/H}}$ of -5.32 kcal/mol (2×-2.66) *vis-à-vis* monosubstituted ethenes, in fact have the value -3.53 kcal/mol, which is quite close to the -3.61 kcal/mol ($-5.32 + 1.69 = -3.63$ kcal/mol) value predicted if the two enthalpies of strain above (*cis*-, +1.04 kcal/mol; 1,1-, +0.65 kcal/mol) acted additively and independently without "buttressing". There is no additional conjugative interaction in tetramethylethene ($\Delta\Delta H_{\text{H}_2} = -26.31$ kcal/mol)!

Surrogates for Conjugative Interaction in Styrene

Two sets of β -alkyl-substituted styrenes have been selected for reevaluation of the enthalpy of conjugative interaction in styrene. Behind this approach lie two plausible assumptions: that interaction of the double bond with the β -alkyl group has not altered its interaction with phenyl; and that steric perturbation in *trans* isomers, if not zero, is well within experimental uncertainties. The set of 1-phenylbutenes (**1a(E)**, **1b(E)**, **1a(Z)**, and **1b(Z)**; series 1 in Chart 1) is otherwise uncomplicated, while the set of 1-phenyl-3-methylbutenes (**2a(E)**, **2b**, **2a(Z)**, and **2c**; series 2 in Chart 1) incorporates two reference standards of differing degrees of substitution, one of which, it is hoped, should have a free energy of formation close enough to that of

the *trans*- β -alkylstyrene of interest to furnish adequately accurate measurements of relevant equilibrium constants. For elucidation of the steric effect of an α -methyl group, the set of five 2-methyl-5-phenylhexenes (series 3, Chart 1) has been selected. The likelihood of residual interaction of the double bond with phenyl in reference compounds **3b** and **3d** is much reduced because they are γ,δ - and δ,ϵ -unsaturated, respectively, relative to the α,β -unsaturated isomers of interest.

In the prior literature, equilibrium between **1a(E)** and **1b(E)** has been established at *single* temperatures by Bateman and Cunneen in methanol at 165 °C catalyzed by sodium methoxide: $\Delta\Delta G = -1.32$ kcal/mol,²³ by Doering and Bragole in dimethyl sulfoxide and $\text{KOC}(\text{CH}_3)_3$ at 55 °C (92.2:6.6; $\Delta\Delta G = -1.72$ kcal/mol),²⁴ and by Carleton at 55 °C in hexamethylphosphoric triamide (HMPT) and $\text{NaOCH}_2\text{CH}_3$ (93.9:3.35; $\Delta\Delta G = -2.18$ kcal/mol).²

Present studies have been made over the range 62–111 °C, in C₆D₆, with a catalyst developed by Wilson and Osborn,^{25a} ruthenium hydridonitrosotris(triphenyl)phosphine^{25b} (Chart 1, series 1, rows 1–3), and over the range 0–97 °C, in HMPT (mp 7.2 °C after several recrystallizations) with 0.1 M $\text{KOC}(\text{CH}_3)_3$ as catalyst (olefin/base, 1:1) (series 1, rows 4–6). Under the latter conditions, the highest temperature that can be usefully employed is limited by the appearance of byproducts and by such a rapid establishment of equilibrium that its position is seriously disturbed during removal and cooling of samples for analysis. That true equilibria have been reached is confirmed by starting from two isomers. To confirm that equilibrium has not been compromised by a kinetically controlled neutralization of an appreciable concentration of intermediary, delocalized carbanion, quenching by D₂O is found to generate products containing negligible amounts of deuterium. To reveal individual experimental uncertainties, the natural logarithm of the percentage of one isomer among all isomers is plotted against the reciprocal of temperature (K). All data and their plots relating to the variation of equilibrium concentrations with temperature in the three series are given as Supporting Information.

Resulting *differences* in free energies [$\Delta\Delta G_{(298^\circ\text{C})}$], enthalpies ($\Delta\Delta_f H$), and entropies ($\Delta\Delta_f S$) of formation with standard deviations are recorded in Chart 1. They pertain to solution and are related to $\Delta\Delta_f H_{\text{gas}}$ by differences in enthalpies of solution and enthalpies of vaporization, which, although not determined, can probably be assumed negligible within experimental uncertainties in such a series of closely related compounds of low polarity. The near identity of equilibrium constants obtained in two such disparate solvents as apolar benzene and aprotic, highly dipolar and polarizable HMPT²⁶ are thought to lend support to the assumption.

Support for the reliability of the experimental method is afforded by the close agreement of the difference between *cis* and *trans* isomers **1b(Z)** and **1b(E)** (+1.06 kcal/mol) and the generic difference (+1.04 kcal/mol; Figure 1); and between the two reference compounds, 1,1-disubstituted **2c** and 1,1,2-trisubstituted **2b** (-1.36 kcal/mol; Chart 1, series 2, row 2), and the difference in enthalpies of hydrogenation (-1.52 kcal/mol; Figure 1)²⁷ of the olefin types.

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(27) The position of equilibrium between **2a(E)** and **2b** ($\Delta\Delta G = +0.06$ kcal/mol) calculated at 165 °C from the experimental $\Delta\Delta_f H$ and $\Delta\Delta_f S$ accords satisfactorily with the value of +0.25 obtained by Bateman and Cunneen at 165 °C.²³

To avoid confusion in discussion, distinction is made between a *theoretical* enthalpy of conjugation ($\Delta\Delta H_{\text{ConjEntH}}$), which is defined as π -electron delocalization alone, and an *empirical* enthalpy of conjugative interaction ($\Delta\Delta H_{\text{ConjInter}}$), which is comprised additionally of such factors as 1,4- π -repulsions, enthalpy of strain, and differences in σ -bond strengths (sp^2 – sp^2 *vis-à-vis* sp^2 – sp^3).²⁸

To generalize a value for $\Delta\Delta H_{\text{ConjInter/Alk}}$ from the difference, for example, between $\Delta\Delta_f H_{1a(E)}$ and $\Delta\Delta_f H_{1b(E)}$, implies an assumption that methyl and ethyl are indistinguishable from each other and alkyl. Subject to this reservation, a weighted mean of -2.55 kcal/mol for $\Delta\Delta H_{\text{ConjInter/Alk}}$ of phenyl *vis-à-vis* alkyl is derived directly (Chart 1, series 1, row 7).

To extract a similar $\Delta\Delta H_{\text{ConjInter/Alk}}$ from $\Delta\Delta_f H$ of **2a(E)**, a disubstituted olefin, and **2b**, a trisubstituted olefin, requires correction by -0.87 ± 0.19 kcal/mol, the difference in enthalpies of hydrogenation of *trans*-1,2-dialkylethenes corresponding to **2a(E)** and 1,1,2-trialkylethenes corresponding to **2b** (Figure 1). A similar extraction from $\Delta\Delta_f H$ of **2a(E)** and **2c** requires correction by $+0.65 \pm 0.14$ kcal/mol, the difference between a *trans*-1,2- and a 1,1-disubstituted alkene. The weighted mean of the two corrected differences, 2.44 ± 0.15 and 2.28 ± 0.14 kcal/mol, respectively, is -2.37 kcal/mol. Agreement with $\Delta\Delta H_{\text{ConjInter/Alk}}$ from series 1, -2.55 kcal/mol, is impressive. The combined result from series 1 and 2 is $\Delta\Delta H_{\text{ConjInter/Alk}} = -2.5 \pm 0.2$ kcal/mol. This is the value recommended for *trans*- β -alkyl-substituted styrenes and styrene itself. Correction by -2.66 kcal/mol generates a value, -5.1 ± 0.2 kcal/mol, for conjugative interaction *vis-à-vis* hydrogen as reference ($\Delta\Delta H_{\text{ConjInter/H}}$).

A cis effect in the conjugated styrenes, **1a(E)** and **1a(Z)** (series 1, row 7: $+2.60$ kcal/mol) and **2a(E)** and **2a(Z)** (series 2, row 2: $+2.37$ kcal/mol), is more than twice the value for the type, *cis*-1,2-dialkyl-substituted olefins ($+1.04$ kcal/mol). The effect is plausibly ascribed to a compromise between maximization of π -electron delocalization by attainment of coplanarity and minimization of nonbonded steric repulsion. Values of $\Delta\Delta H_{\text{ConjInter/Alk}}$ for *cis*- β -alkyl-substituted styrenes are correspondingly lower: -1.01 kcal/mol from **1a(Z)** (series 1, row 7) and -1.11 kcal/mol from **2a(Z)** ($+0.80$ corrected by -1.91 kcal/mol, Figure 1). The mean value for $\Delta\Delta H_{\text{ConjInter/H}}$ is -2.7 kcal/mol (compare the value from Taskinen for *cis*-1-phenylpropene, -2.94 kcal/mol).¹⁶

Steric Factor in α -Substituted Styrenes

In the 2-phenyl-5-methylhexenes (Chart 1, series 3), the reference compound, **3b**, is trisubstituted as is **3a(E)** and **3a(Z)**, while **3d** like **3c** is 1,1-disubstituted. As in series 1, $\Delta\Delta H_{\text{ConjInter/Alk}}$ is derived directly from values of $\Delta\Delta_f H$ without correction for differences in substitution. Establishment of stereochemistry in **3a(E)** and **3a(Z)** is based, first, on comparison of the chemical shifts of their β -hydrogens at 5.80 and 5.48 ppm, respectively, with the two β -hydrogens *cis* and *trans* to the phenyl group in styrene (5.3 vs 4.8), *p*-chlorostyrene (5.73 vs 5.28), α -methylstyrene (5.34 vs 4.99), and *p*-isopropylstyrene (5.32 vs 4.99), on comparison with the vinyl hydrogens in *trans*- (7.03) and *cis*- (6.57) stilbenes, and the β -hydrogens in **1a(E)** (6.10) and **1a(Z)** (5.53), and **2a(E)** (6.08) and **2a(Z)** (5.39); second, by observation of a small but consistent nuclear Overhauser effect upon saturation of the aromatic hydrogens and the α -methyl groups; and third, differences in UV spectra²⁹

and free energy at equilibrium³⁰ quite comparable to those found for (*E*)- and (*Z*)-2-phenylbut-2-ene.

Equilibrations over the range 81–154 °C in HMPT/KOC-(CH₃)₃ are unexceptional, although a declining recovery limits the highest practicable temperature. Equilibrium constants involving **3a(E)**, **3a(Z)**, and **3b** fall within the experimentally favorable range of $2 > \ln K > -2$. Values for $\Delta H_{\text{ConjInter/Alk}}$ are derived directly by comparisons of **3a(E)** with **3b**, -1.1 kcal/mol, **3c** with **3d**, -0.4 kcal/mol, and **3a(Z)** with **3b**, 0.0 kcal/mol. Corresponding values of $\Delta H_{\text{ConjInter/H}}$ are -3.7 , -3.1 , and -2.7 kcal/mol, respectively. The sensitivity to what intuitively seem to be very small steric differences in **3a(E)** and **3c** is remarkable.

The *cis*–*trans* increment in the **3a** pair deserves comment. **3a(E)** contains a conventional unit of *cis* strain (methyl vs isobutyl: $+1.04$ kcal/mol), which should vanish in passing to **3a(Z)**, but in fact is more than compensated by an *increase* of $+1.08$ kcal/mol. This striking difference between expectation and fact in **3a(E)** and **3a(Z)** of $+2.12$ kcal/mol is doubtless steric in origin, but how it should be allocated between a decrease in π -electronic factor attributable to significant divergence from coplanarity and nonbonded steric repulsion between twisted phenyl and isobutyl is elusive.

Entropy is not a negligible factor. In series 1, it translates to a contribution of 0.5–0.7 kcal/mol to the differences in free energy of **1a(E)** and **1b(E)** while in series 2 it translates to 1.0 kcal/mol or more; and in series 3, entropy contributes 0.3–0.4 kcal/mol to the differences between free energies and enthalpies.

Translation into Enthalpies of Formation

Values of $\Delta\Delta_f H_{\text{exp}}$ can be transformed into useful enthalpies of formation by focusing on the unconjugated isomers—**1a(E)**, **2b** and **2c**, and **3b** and **3d**. Their enthalpies of formation can be estimated from compounds already in the literature in a straightforward and reliable manner. The preferred ways involve (i) the empirically based method of group equivalents of Franklin^{31a} as elaborated by Benson;^{31b,c} (ii) extraction of a value for the change in enthalpy of formation, $\Delta\Delta_f H^\circ$, on replacement of a hydrogen in a methyl group by phenyl and application of this value to the appropriate alkene; and (iii) subtraction from the appropriate phenylalkane of the appropriate enthalpy of hydrogenation given in Figure 1. From these estimates, a mean value for $\Delta_f H^\circ_{\text{est}}$ of *trans*-1-phenylbut-2-ene (**1b(E)**), $+24.32 \pm 0.23$ kcal/mol, can be derived (series 1, row 8).³² For 2-methyl-4-phenylbut-2-ene (**2b**) and 2-methyl-4-phenylbut-1-ene (**2c**), mean values for $\Delta_f H^\circ_{\text{est}}$ of $+16.62 \pm 0.37$ and $+18.49 \pm 0.33$ kcal/mol, respectively, are derived (series 2, row 4).³³ Finally, for 2-methyl-5-phenylhex-2-ene (**3b**) and 2-methyl-5-phenylhex-1-ene (**3d**), mean values for $\Delta_f H^\circ_{\text{est}}$ of $+16.62 \pm 0.37$ and $+18.49 \pm 0.33$ kcal/mol, respectively, are obtained (series 3, row 4).³⁴ Addition of the appropriate values

(30) Fort, A. W.; Girard, C. A. *J. Am. Chem. Soc.* **1961**, *83*, 3449–3453.

(31) (a) Franklin, J. L. *Ind. Eng. Chem.* **1949**, *41*, 1070–1076. (b) Benson, S. W.; Cruikshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Walsh, R. *Chem. Rev.* **1968**, *68*, 1513–1524. (c) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

(32) (i) Benson value (p 272):^{31c} $+24.70$ kcal/mol. (ii) For the change in enthalpy of formation when benzene and CH₃R are dehydrogenated to C₆H₅CH₂R ($\Delta\Delta_f H^\circ(\text{CH}_3\text{R}-\text{C}_6\text{H}_5\text{CH}_2\text{R})$, a mean value of $+26.98 \pm 0.14$ kcal/mol can be derived from four pairs of $\Delta_f H^\circ$ (in kcal/mol) in the literature:³ ethylbenzene ($+7.15$)/ethane (-20.03); 1-phenylpropane ($+1.89$)/propane (-25.02); 1-phenylbutane (-3.13)/*n*-butane (-30.02); 2-methyl-1-phenylpropane (-5.14)/2-methylpropane (-32.07). Application of this value to *trans*-butene (-2.72 kcal/mol) leads to $+24.26$ kcal/mol. (iii) $\Delta_f H^\circ$ - (1-phenylbutane) = $-3.13^5 + 27.25$ (Figure 1) = $+24.12$ kcal/mol; alternatively, $\Delta_f H^\circ$ (*n*-butane) = $30.02 + 26.98 + 27.25 = +24.21$ kcal/mol. A mean value for $\Delta_f H^\circ$ of *trans*-1-phenylbutene-2 (**1b(E)**) is $+24.32 \pm 0.26$ kcal/mol.

(28) Dewar, M. J. S.; Schmeising, H. N. *Tetrahedron* **1959**, *5*, 166–178. Dewar, M. J. S.; Schmeising, H. N. *Tetrahedron* **1960**, *9*, 96–120.

(29) Cram, D. J. *J. Am. Chem. Soc.* **1949**, *71*, 3883–3889.

of $\Delta\Delta_f H_{\text{exp}}$ (series **1**, row 7; **2**, row 2; and **3**, row 2) to these reference hydrocarbons generates estimated enthalpies of formation, $\Delta_f H^{\circ}_{\text{est}}$, of the remaining compounds in the series. In series **2** and **3**, two sets of nearly identical $\Delta_f H^{\circ}_{\text{est}}$ can be generated, depending on which of two reference compounds is selected.

These new thermochemical data are potentially useful for evaluating the accuracy of quantum and molecular mechanical approaches to enthalpies of formation. We have applied the most recent version of the MMEVBH program of Roth,¹³ which combines the MM2 program of Allinger as modified in MM2ERW³⁵ with the program of the extended valence bond Hamiltonian developed by Maynau and Malrieu³⁶ and the MM3 program of Allinger.³⁷ Corrections for TOP (torsional) and POP (Boltzmann) have not been made.³⁸ Although this omission affects the calculated values of enthalpies of formation, except as noted, it has little effect on the differences. No exhaustive evaluation is contemplated here.³⁹

Comparisons of cis–trans isomers seems most favorable, as they involve “*isoBensonian*” geometrical isomers⁴⁰ and no significant corrections for POP and TOP. For the comparison of **1b(E)** and **1b(Z)**, both methods do very well, while MMEVBH does rather less well than MM3 in the comparison of **1a(E)** and **1a(Z)** [Chart 1, series **1**: row 7, $\Delta\Delta_f H_{\text{exp}} = -2.60$ kcal/mol, versus row 9, $\Delta\Delta_f H^{\circ}_{\text{MMEVBH}} = -1.85$ kcal/mol, and row 11, $\Delta\Delta_f H^{\circ}_{\text{MM3}} = -2.45$ kcal/mol], and in the comparison of **2a(E)** and **2a(Z)** [experimental difference of -2.37 kcal/

(33) (i) Benson values for $\Delta_f H^{\circ}_{\text{est}}$ (**2b**), +16.25 kcal/mol, and for $\Delta_f H^{\circ}_{\text{est}}$ (**2c**), 18.79 kcal/mol. (ii) From known heats of formation (in kcal/mol) of 2-methylbut-2-ene (-9.99) and 2-methylbut-1-ene (-8.44),⁵ the addition of ($\Delta\Delta_f H^{\circ}(\text{CH}_3\text{R}\rightarrow\text{C}_6\text{H}_5\text{CH}_2\text{R})$, +26.98, leads to $\Delta_f H^{\circ}_{\text{est}}$ (**2b**), +16.99, and $\Delta_f H^{\circ}_{\text{est}}$ (**2c**), +18.54, respectively. (iii) Addition of $\Delta\Delta_f H^{\circ}(\text{CH}_3\text{R}\rightarrow\text{C}_6\text{H}_5\text{CH}_2\text{R})$ ³² to 2-methylbutane (-36.74 kcal/mol)⁵ leads to $\Delta_f H^{\circ}_{\text{est}}$ (2-methyl-4-phenylbutane) of -9.76 kcal/mol. Whence additions of the heats of dehydrogenation of 1,1,2-trialkyl-substituted ethenes (Figure 1, +26.38 kcal/mol) and 1,1-dialkyl-substituted ethenes (+27.90 kcal/mol), respectively, lead to $\Delta_f H^{\circ}_{\text{est}}$ (**2b**) of +16.62 and $\Delta_f H^{\circ}_{\text{est}}$ (**2c**) of +18.14 kcal/mol. Mean values of +16.62 \pm 0.37 and +18.49 \pm 0.33 kcal/mol are derived for $\Delta_f H^{\circ}_{\text{est}}$ (**2b**) and $\Delta_f H^{\circ}_{\text{est}}$ (**2c**), respectively.

(34) (i) Benson values for $\Delta_f H^{\circ}_{\text{est}}$ (**3b**), +5.60 kcal/mol, and for $\Delta_f H^{\circ}_{\text{est}}$ (**3c**), +7.54 kcal/mol. (ii) A mean value (in kcal/mol) for $\Delta\Delta_f H^{\circ}(\text{RCH}_2\text{R}'\rightarrow\text{C}_6\text{H}_5\text{CHRR}')$ of +25.78 \pm 0.26 is derived from three pairs of $\Delta_f H^{\circ}$ in the literature:⁵ isopropylbenzene(+25.98)/propane; *sec*-butylbenzene(+25.86)/*n*-butane; and phenylcyclohexane(+25.49)/cyclohexane. From ΔH_{H_2} of 2-methylhex-2-ene (-26.00 kcal/mol) and 2-methylhex-2-ene (-27.68 kcal/mol)²⁰ to 2-methylhexane ($\Delta_f H^{\circ} = -46.51$ kcal/mol)⁵ and addition of the increment, +25.78 kcal/mol, $\Delta_f H^{\circ}_{\text{est}}$ of **3b** and **3d** of +5.27 and 6.95 kcal/mol, respectively, are derived. (iii) Addition of the increment, +25.78 kcal/mol, to the $\Delta_f H^{\circ}$ of 2-methylhexane (-46.51 kcal/mol)⁵ leads to $\Delta_f H^{\circ}_{\text{est}}$ of the common product of hydrogenation, 2-methyl-5-phenylhexane, of -20.73 kcal/mol. Dehydrogenation based on the appropriate enthalpies of hydrogenation of the type (Figure 1) leads to $\Delta_f H^{\circ}_{\text{est}}$ of **3b** and **3d** of +5.65 and 7.17 kcal/mol, respectively. Mean values of +5.51 \pm 0.21 and +7.22 \pm 0.30 kcal/mol are included in Chart 1, series **3**, row 4.

(35) Roth, W. R.; Adamczak, O.; Breuckmann, R.; Lennartz, H.-W.; Boese, R. *Chem. Ber.* **1991**, *124*, 2499–2521.

(36) Säid, M.; Maynau, D.; Malrieu, J.-P.; Garcia Bach, M.-A. *J. Am. Chem. Soc.* **1984**, *106*, 571–579.

(37) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551–8566.

(38) We express our sincere appreciation to Professor Wolfgang Roth for having checked both the EVBH and MM3 calculations. The EVBH program is available on application to Prof. Dr. W. R. Roth, Ruhr-Universität Bochum, Organische Chemie, Postfach 10 21 48, D-44780 Bochum, Germany. He notes that TOP and POP corrections to the MM3 results have not been made, and that, although Allinger has not discussed this matter explicitly in connection with MM3, one can infer from published examples that a correction for (TOP + POP) of 0.75 kcal/mol has been made for each freely rotating bond (i.e., <7 kcal/mol barrier; excluding bonds to methyl). In **2c**, **3c**, and **3d** this correction would raise the calculated values of $\Delta\Delta_f H^{\circ}$ by 0.75 kcal/mol, all others remaining unchanged.

(39) “. . . it’s one of those things that once you have done it with supervision of someone who really understands it, then you will understand it. But working from the literature, it is not so easy.”

(40) Compounds describable by identical summations of group equivalent values. Indeed, the entire evaluation of several molecular methods focuses on differences of conformational energies.⁴¹

mol (Chart 2, row 2); calculated differences, -1.49 (MMEVBH, row 5) and -2.30 kcal/mol (MM3, row 7)]. In the comparison of **3a(E)** and **3a(Z)**, MMEVBH is substantially superior to MM3: experimental, -1.08 kcal/mol (Chart 3, row 2); MMEVBH, -0.62 kcal/mol (row 5); MM3, -0.10 kcal/mol.

The experimental value for $\Delta\Delta H_{(\text{ConjInter/Alk})}$ (**1a(E)** minus **1b(E)**, Chart 1, row 7: -2.55 kcal/mol) compares with the values of -1.47 kcal/mol calculated by MMEVBH (row 9) and of -1.13 kcal/mol by MM3 (row 11). Comparison between **2a(E)** and **2b** is unsatisfactory, MMEVBH at least being in the right direction. Other comparisons are left to the reader. There is an apparent need for a critical evaluation of computational methods⁴¹ in the prediction of the enthalpic component of equilibria.

Taken together, the susceptibility of enthalpy of conjugative interaction to the cis effect and α -substitution should serve as a warning against uncritical application of a single value for styrene conjugation. The ultimate usefulness of a concept of “intrinsic” π -electron delocalization (enthalpy of conjugation) in styrenes generally will depend on the ability to estimate accurately the steric factor and the availability of a good force field for the phenyl–double bond dihedral angle. There seems to be considerable room for improvement in the continuing effort to gain intellectual control over the connection between structure and thermochemistry. At the interface of experiment and theoretical constructions, there remains great need for congruity at least at the level of ± 1.0 kcal/mol proposed by Michael Dewar for “chemical accuracy” over a quarter of a century ago,⁴² if not more realistically for the immediate future at the level of ± 0.3 kcal/mol.

Steric Effect of *o*-Methyl Groups

Interference with the attainment of coplanarity between the benzene ring and the double bond can also be explored by introducing methyl groups at positions 2' and 6'.^{2,43} These studies have included examination of the 1-(2',4'-dimethylphenyl)- and the 1-(2',4',6'-trimethylphenyl)-*n*-butenes and *n*-pentenes. Because equilibrations have been established at a *single* temperature only, 90 °C in (unpurified) HMPT with sodium ethoxide or potassium *tert*-butoxide as catalyst, discussion of the results collected in Chart 2 is limited. Results of calculations by the two molecular mechanical programs above are also included.

Introduction of a second *o*-methyl group into **4a(E)** to generate **5a(E)** attenuates the free energy of conjugation in **4a(E)** by 0.9 kcal/mol consistent with the expected greater deviation from coplanarity (bond angles indicated in the formulas come from MMEVBH calculations). A similar attenuation in $\Delta\Delta G$ is seen in the comparison of the cis–trans pairs, **4a(E)** and **4a(Z)**, and **5a(E)** and **5a(Z)**. Parenthetically, the slightly greater difference in $\Delta\Delta G$ in the pair **1a(E)** and **1b(E)** (~ -2.0 kcal/mol; Chart 1, series **1**, rows 2 and 4) compared to that in **4a(E)** and **4b(E)** (-1.57 kcal/mol; Chart 2) is in good agreement with the finding of Hine and Skogland in the *intramolecular* competition in the system of 1-phenyl-3-(*o*-tolyl)propenes ($\Delta\Delta G_{353} = -0.46$ kcal/mol).⁴⁴

In series **6**, **7**, and **8**, the *o*-methyl factor has been combined with the α -methyl factor. The near identity of series **7** and **8** confirms that a methyl group in the 4' position is without effect. This result agrees with that of Bushby and Ferber in the series

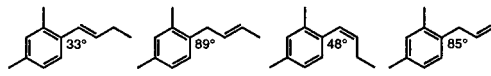
(41) For example: Gundertofte, K.; Liljefors, T.; Norrby, P.-O.; Pettersson, I. *J. Comput. Chem.* **1996**, *17*, 429–449.

(42) Dewar, M. J. S. *XXIIIrd International Congress of Pure and Applied Chemistry*; Butterworths: London, 1971; Vol. 1, pp 1–30.

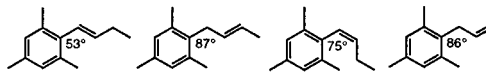
(43) Proctor, George R., unpublished work on the 1-phenyl-3-mesitylpropene system; Yale University, 1963, supported by the Norman Fund.

(44) Hine, J.; Skogland, M. J. *J. Org. Chem.* **1982**, *47*, 4758–4766.

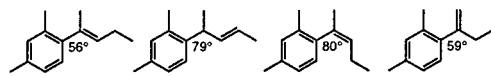
Chart 2



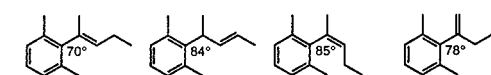
Series 4	4a(E)	4b(E)	4a(Z)	4b(Z)
HMPT, NaOEt				
1 equil(363 K)	82.3%	9.60%	5.97%	1.54%
2 $\Delta\Delta G_{(363\text{ K})}$	-1.57	0.00	+0.37	+1.32
3 $\Delta_f H^{\circ}_{\text{EVBH}}$	+6.25	+7.69	+7.89	+8.90
4 $\Delta\Delta_f H^{\circ}_{\text{EVBH}}$	-1.44	0.00	+0.20	+1.21
5 $\Delta_f H^{\circ}_{\text{MM3}}$	+5.66	+6.61	+7.40	+7.46
6 $\Delta\Delta_f H^{\circ}_{\text{MM3}}$	-0.95	0.00	+0.79	+0.85



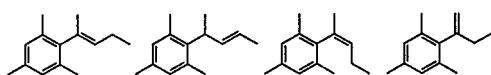
Series 5	5a(E)	5b(E)	5a(Z)	5b(Z)
HMPT, KO-t-Bu				
1 equil(363 K)	53.3%	21.6%	21.4%	3.76%
2 $\Delta\Delta G_{(363\text{ K})}$	-0.65	0.00	+0.01	+1.26
3 $\Delta_f H^{\circ}_{\text{EVBH}}$	+8.23	+8.99	+9.61	+10.24
4 $\Delta\Delta_f H^{\circ}_{\text{EVBH}}$	-0.76	0.00	+0.62	+1.25
5 $\Delta_f H^{\circ}_{\text{MM3}}$	+7.43	+7.57	+8.07	+8.52
6 $\Delta\Delta_f H^{\circ}_{\text{MM3}}$	-0.14	0.00	+0.50	+0.95



Series 6	6a(E)	6b(E)	6a(Z)	6c
HMPT, KO-t-Bu				
1 equil(363 K)	33.4%	2.48%	59.8%	3.55%
2 $\Delta\Delta G_{(363\text{ K})}$	-1.88	0.00	-2.30	-0.26
3 $\Delta_f H^{\circ}_{\text{EVBH}}$	+0.10	+4.70	+0.47	+1.11
4 $\Delta\Delta_f H^{\circ}_{\text{EVBH}}$	-4.60	0.00	-4.23	-3.59
5 $\Delta_f H^{\circ}_{\text{MM3}}$	-1.07	+3.66	-1.42	+0.54
6 $\Delta\Delta_f H^{\circ}_{\text{MM3}}$	-4.73	0.00	-5.08	-3.12



Series 7	7a(E)	7b(E)	7a(Z)	7c
HMPT, KO-t-Bu				
1 equil(363 K)	22.3%	0.11%	75.8%	1.91%
2 $\Delta\Delta G_{(363\text{ K})}$	-3.83	0.00	-4.71	-2.05
3 $\Delta_f H^{\circ}_{\text{EVBH}}$	+0.85	+6.83	+0.62	+3.45
4 $\Delta\Delta_f H^{\circ}_{\text{EVBH}}$	-5.98	0.00	-6.21	-3.38
5 $\Delta_f H^{\circ}_{\text{MM3}}$	-0.95	+5.56	-1.33	+1.42
6 $\Delta\Delta_f H^{\circ}_{\text{MM3}}$	-6.51	0.00	-6.89	-4.14



Series 8	8a(E)	8b(E)	8a(Z)	8c
HMPT, KO-t-Bu				
1 equil(363 K)	22.3%	0.13%	75.2%	1.97%
2 $\Delta\Delta G_{(363\text{ K})}$	-3.65	0.0	-4.59	-1.90

of 1-phenyl-3-(*p*-tolyl)propenes.⁴⁵ Assignment of configuration to the *cis*–*trans* pairs in series 6, 7, and 8, illustrated in detail for 8a(E) and 8a(Z) in Figure 5 included in the Supporting Information, is based on analogy with chemical shifts in the NMR spectra of styrene and *o*-methylstyrene, in which the vinyl hydrogens *trans* to the benzene ring are upfield of the *cis* hydrogen but downfield in 2',4',6'-trimethylstyrene.

In series 7 (and 8), the second *o*-methyl group appears to have occasioned a dramatic increase in $\Delta\Delta G_{\text{ConjInter/alk}}$, *vis-à-*

vis series 6. On the assumption that this difference would persist if differences in enthalpy had been measured, this apparent increase is more likely the result of a large increase in steric factor in 7b(E) than an enhancement of π -electron delocalization in 7a(Z)! A qualitative explanation is possibly to be found in the inability of substituents on the sp^3 α -carbon to escape steric interference from the methyl groups at 2' and 6' positions of the benzene ring. How far out of the plane awaits crystallographic analysis; meanwhile the dihedral angles revealed by MM at globally minimized steric energies in system 7 are close to 90°.

Conclusions

The main lesson is clear: reliance on a single value for conjugative interaction in styrene is quite unjustified for predictive purposes in more complicated systems. The *cis* effect, α -substituents, and *ortho* substituents lead to marked and variable attenuations of conjugative interaction. A second lesson teaches the inadequacy of equating enthalpies and free energies of conjugative interaction: entropies can be large and adversely influential on the position of equilibrium of conjugated isomers relative to their unconjugated isomers. Although it may be useful to define an intrinsic enthalpy of π -electron delocalization, empirical conjugative interaction is not its measure, but is rather a composite thermochemical quantity thought to consist of an interplay between an enthalpy-raising, nonbonded steric interaction *per se* and its attenuation of enthalpy-lowering π -electron delocalization by enforcement of a deviation from coplanarity.

At the present time, this interplay seems not to be well calculable by molecular mechanical programs with an accuracy appropriate to a useful prediction of positions of equilibria. The thermochemical data brought to light here on three sets of isomeric compounds of simple structure offer one of few opportunities to test the accuracy of molecular mechanical programs that is neither redundant nor has already been consumed by parametrization.⁴⁶ Additional sets are desirable.

Experimental Section

General Procedures. NMR spectra are determined on Bruker AM Series 250, 300, 400, or 500N in C_6D_6 unless otherwise noted, and are referenced to $\text{C}_6\text{D}_5\text{H}$ and reported in ppm, δ scale; coupling constants (*J*) are reported in Hz. Spin–lattice relaxation times (T_1) are determined by the inversion recovery method. IR spectra, recorded on a Mattson Galaxy Series FTIR 3000, are measured, unless otherwise noted, in KBr pellets and reported in cm^{-1} . UV spectra are measured on a Hewlett Packard 8452A diode array spectrophotometer in spectrograde hexane and are reported as λ_{max} in nm ($\log \epsilon$). GC-EIMS (70 eV) are obtained on a Hewlett Packard 5890 Series II gas chromatograph (HP 5 MS, 30 m \times 0.25 mm) and a Hewlett Packard 5972 Series mass selective detector and are reported as *m/z* and intensity (as %) of major peak.

Analytical GC are effected on a Hewlett Packard 5890 A gas chromatograph with J & W Scientific columns: (A) Megabore, DB-1, 30 m \times 1.5 mm; and (B) DB 1701, 30 m \times 1.0 mm. Preparative GLC are performed on a Varian Aerograph Model 90-P, column C: 20% Carbowax on Anakrom AS 50/60; 3 m, i.d. 5 mm, 20 psi He (2 mL/s); injector 175 °C, column 175 °C, detector 220 °C unless otherwise noted. Melting points are uncorrected. Solvents are redistilled before use: THF from sodium/benzophenone; mixed hexanes and ethyl ether from LiAlH_4 ; CHCl_3 and CH_3CN from CaCl_2 ; methanol from Mg; pyridine and 2,6-lutidine from KOH; *tert*-butyl alcohol from CaH_2 ; and CH_3I through a column filled with copper wire.

Materials. In series 1–3, Wittig reactions are carried out by preparing the ylide by addition of a 2.5 M solution of *n*-butyllithium (10% molar excess) in hexanes under argon over a period of 1 h to a

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vigorously stirred suspension of the apposite triphenylphosphonium halide in anhydrous THF maintained at 0 °C in an ice/water bath. After the mixture is stirred for an hour at 0 °C, aldehyde or ketone in anhydrous THF is added over a 1-h period. The reaction mixture is warmed to room temperature and stirred for 1.5 h. Workup procedure A includes filtration over a bed of Celite (pentane), concentration *in vacuo* (<15 °C), and subsequent purification over 10 g of silica (pentane); procedure B includes concentration *in vacuo*, thorough extraction of the residue with hexanes (total, 500 mL), filtration, drying over K₂CO₃, and evaporation of solvent to leave an oil, which is then purified by vacuum distillation.

Grignard reagents are prepared in the usual manner, treated with aldehyde or ketone under argon (<40 °C), and worked up conventionally.

Series 1. (E)-1-Phenylbut-2-ene (1b(E)). 1b(E) was obtained from (Aldrich Chemical Co.) and purified by distillation, but it still remained contaminated by 5% of 1b(Z): ¹H NMR (300 MHz) 7.25–7.00 (m, 5H), 5.51 (m, 1H), 5.37 (m, 1H), 3.19 (d, 2H, *J* = 6.5, H-1), 1.54 (dm, 3H, *J* = 5.9, H-4).

(E)-1-Phenylbut-1-ene (1a(E)). This compound is prepared from 1.5 g of 1b(E) by equilibration in 10 mL of a 0.05 M solution of potassium *tert*-butoxide in HMPT in a Schlenk flask with stirring under argon for 30 min at room temperature. The mixture is then worked up by quenching with 50 mL of water and extraction with 100 mL of pentane. The extract is washed twice with H₂O (50 mL each) and 50 mL of brine and concentrated *in vacuo* at 0 °C. Distillation then affords 0.9 g (60%) of 1a(E) in a purity of 96% (GC): ¹H NMR (500 MHz) 7.25–7.00 (m, 5H), 6.30 (d, 1H, *J* = 15.8, H-1), 6.10 (dt, 1H, *J* = 6.6, H-2), 2.04 (m, 2H, *J* = 7.5, 1.4, H-3), 0.95 (t, 3H, H-4).

(E)- and (Z)-1-Phenylbut-1-ene (1a(E) and 1a(Z)). 1a(E) and 1a(Z) are prepared by the Wittig reaction (*vide supra*) from 16.5 g of isopropyltriphenylphosphonium bromide and 2.8 g of benzaldehyde, which after distillation *in vacuo* affords 2.7 g (77%) of a 43:57 mixture of 1a(E) and 1a(Z): ¹H NMR (500 MHz) 7.25–7.00 (m, 5H), 6.37 (d, 1H, *J* = 11.6, H-1), 5.53 (dt, 1H, *J* = 7.3, H-2), 2.21 (dm, 2H, *J* = 7.5, 1.8, H-3), 0.89 (t, 3H, H-4). 1a(Z) has also been prepared by hydrogenation of 1-phenylbutyne⁴⁷ with 10% Pd on CaCO₃ in methanol (interrupted after the uptake of 0.95 mol equiv of H₂).

4-Phenylbut-1-ene (1c). A sample from Aldrich Chemical Co. is purified by distillation: ¹H NMR (300 MHz) 7.20–6.95 (m, 5H), 5.73 (m, 1H, H-2), 4.98 (dm, 1H, H-1), 4.93 (dm, 1H, H-1), 2.52 (t, 2H, *J* = 7.8, H-4), 2.21 (m, 2H, H-3).

Series 2. 1-Phenyl-3-methylbut-1-enes (2a(E) and 2a(Z)). These olefins are obtained by a Wittig reaction between benzyltriphenylphosphonium chloride (33.2 g) and isobutyraldehyde (3.7 g). Vacuum distillation (bp 40 °C/0.25 mm) yields 4.62 g (31.6 mmol, 62%) of a 76:24 mixture of 2a(E) and 2a(Z). Separation of 1.8 g of product into the pure isomers by preparative GLC (column C) and subsequent distillation *in vacuo* provides 0.39 g of 2a(E) and 0.88 g of 2a(Z), the latter also having been prepared by the following sequence, alkylation of phenylacetylene⁴⁸ to phenylisopropylacetylene and partial hydrogenation of the latter⁴⁹ (for details, see Carleton dissertation).² 2a(E): ¹H NMR (500 MHz) 7.26 (d, 2H), 7.14 (t, 2H), 7.04 (t, 1H), 6.30 (d, 1H, *J* = 16, H-1), 6.08 (dd, 1H, *J* = 6.9, H-2), 2.29 (m, 1H, *J* = 6.8, H-3), 0.99 (d, 6H, H-4); IR 3100–2800, 1651, 1597, 1493, 966, 789, 698; UV 252 (4.15), 210 (4.11); GC-MS 146 (37) [M⁺], 131 (100) [M⁺ – CH₃], 91 (42) [C₇H₇⁺]. 2a(Z): ¹H NMR (500 MHz): 7.25 (d, 2H), 7.16 (t, 2H), 7.05 (t, 1H), 6.31 (d, 1H, *J* = 11.6, H-1), 5.39 (dd, 1H, *J* = 10.2, H-2), 2.90 (m, 1H, *J* = 6.6, H-3), 0.93 (d, 6H, H-4); IR 3100–2800, 1598, 1494, 762, 789, 697; UV 242 (4.09), 208 (4.10).

3-Methyl-1-phenylbut-2-ene (2b). This compound is prepared by the dehydration of 2-methyl-4-phenylbutan-2-ol (obtained from benzylacetone and ethereal methylolithium) at 0 °C: bp 76 °C/0.1 mm; mp 44 °C from petroleum ether at –80 °C; ¹H NMR (300 MHz) 7.25–7.05 (m, 5H), 2.59 (m, 2H), 1.58 (m, 2H), 1.03 (s, 6H), 0.85 (s, 1H, OH). A solution of carbinol (5.0 g) in 80 mL of toluene containing 0.4 g of *p*-toluenesulfonic acid is heated for 5 h under reflux with

separation of evolved water. The usual workup (washing with saturated NaHCO₃ (three 50-mL portions) and brine, drying over anhydrous K₂CO₃, filtering, and concentrating *in vacuo* at 0 °C), affords, after distillation, 3.8 g (86%) of an 84:16 mixture of 2b and 2c (bp 40 °C/0.1 mm). Pure 2b is obtained by preparative GLC (column C) and subsequent vacuum distillation (0.8 g from 1.2 g): ¹H NMR (300 MHz) 7.2–7.0 (m, 5H), 5.34 (tm, 1H, *J* = 7.3, 1.5), 3.26 (d, 2H), 1.63 (d, 3H), 1.55 (s, 3H); IR 3100–2800, 1604, 1494, 740, 697; UV 252 (2.88), 208 (4.07).

2-Methyl-4-phenylbut-1-ene (2c). Preparation by a Wittig reaction from methyltriphenylphosphonium bromide (30.5 g) and 4-phenyl-2-butanone (Aldrich; 7.62 g) and distillation (bp 40 °C/0.25 mm) yields 4.98 g (66%) of 2c as a colorless liquid: ¹H NMR (250 MHz) 7.0–7.2 (m, 5 H), 4.77 (m, 1H, H-1), 4.74 (m, 1H, H-1), 2.62 (t, 2H, *J* = 8.0, H-4), 2.19 (t, 2H, H-3), 1.61 (s, 3H); IR 3100–2800, 1650, 1604, 1496, 888, 745, 698; UV 262 (2.11), 208 (3.92), 200 (3.99).

Series 3. (E)- and (Z)-2-Phenyl-5-methylhex-2-ene (3a(E) and 3a(Z)). (1-Phenylethyl)triphenylphosphonium bromide is prepared from 26.2 g of triphenylphosphine and 18.5 g of 1-phenylethyl bromide (Aldrich Chemical Co.) in 30 mL of toluene under reflux for 10 h: colorless crystals; 40.0 g (89%); mp 222 °C; ¹H NMR (250 MHz, CDCl₃) 7.75–7.45 (m, 15H), 7.20–7.00 (m, 5H), 6.48 (m, 1H, *J* = 7.0, 7.0), 1.72 (dd, 3H, *J* = 19.1). Wittig reaction (*vide supra*) [40 g of phosphonium bromide and 4.7 g of 3-methylbutanal (Aldrich Chemical Co.)] affords a yellow oil, bp 65 °C/0.1 mm, 5.43 g (57%), as an 84:16 mixture of 3a(E) and 3a(Z). This mixture (2 g) is separated by preparative GLC (column C; injector 180 °C; column, 185 °C; detector, 185 °C) and subsequent vacuum distillation to give 0.95 g of 3a(E) and 0.44 g of 3a(Z). 3a(E): ¹H NMR (500 MHz) 7.34 (d, 2H), 7.18 (t, 2H), 7.09 (t, 1H), 5.80 (tq, 1H, *J* = 7.4, 1.2), 1.99 (t, 2H), 1.90 (s, 3H), 1.61 (sept, 1H, *J* = 6.7), 0.89 (d, 6H); ¹³C NMR (125.8 MHz) 145.19, 136.31, 128.94, 128.04, 127.27, 126.59, 38.71, 29.96, 23.08, 16.56; IR 3100–2800, 1598, 1494, 755, 696; UV 246 (4.08), 210 (4.04); GC-MS 174 (8) [M⁺], 131 (100) [M⁺ – C₃H₇], 118 (15) [C₉H₁₀⁺], 91 (55) [C₇H₇⁺]. 3a(Z): ¹H NMR (500 MHz) 7.17 (m, 4H), 7.06 (t, 1H), 5.48 (td, 1H, *J* = 7.3, 1.3), 2.00 (t, 3H), 1.94 (m, 2H, *J* = 1.2), 1.55 (sept, 1H, *J* = 6.7), 0.72 (d, 6H); ¹³C NMR (125.8 MHz) 143.37, 137.82, 128.86, 128.85, 127.33, 127.17, 38.96, 29.79, 26.35, 22.93; IR 3100–2800, 1600, 1494, 762, 700; UV 236 (3.80), 204 (4.07); GC-MS 174 (10) [M⁺], 131 (100) [M⁺ – C₃H₇], 118 (25) [C₉H₁₀⁺], 91 (53) [C₇H₇⁺].

2-Methyl-5-phenylhex-1-ene (3d). (a) 1-Bromo-2-phenylpropane is prepared by a modification of the procedure of Brown and Lane.⁵⁰ To a solution of 35.5 g (0.3 mol) of α -methylstyrene in 90 mL of anhydrous THF is added 100 mL (0.1 mol) of a 1 M solution of BH₃ in anhydrous THF under argon over a period of 1 h (0–5 °C). After being stirred for 5 h at 25 °C, the reaction mixture is carefully quenched with 2 mL of methanol and cooled to –10 °C. Addition of 20 mL (0.4 mol) of bromine, followed by 100 mL (0.5 mol) of a 25% solution of NaOCH₃ in CH₃OH (*T* < 0 °C) with stirring for 30 min, addition of saturated aqueous K₂CO₃, thorough extraction with hexanes (4 × 150 mL), washing the combined hexane extracts with water (3 × 100 mL) and 100 mL of brine, drying the solution over MgSO₄, and finally filtering and concentrating the solution *in vacuo* affords a yellow liquid (33 g) consisting of a 75:25 mixture of 1-bromo-2-phenylpropane and 2-phenylpropanol. This mixture is heated under reflux in 200 mL of hexanes with 1.2 g of LiAlH₄ for 1.5 h, cooled, filtered, and concentrated *in vacuo* to a crude product, which is purified by vacuum distillation to afford 19.5 g (33%, bp 70 °C/0.1 mm) of 1-bromo-2-phenylpropane: ¹H NMR (250 MHz) 7.15–6.80 (m, 5H), 3.17 (dd, 1H, *J* = 9.8, 6.0), 3.03 (dd, 1H, *J* = 8.0), 2.77 (m, 1H, *J* = 6.9), 1.11 (d, 3H). The bromide (12.2 g) is converted to its Grignard reagent (*vide supra*), treated with 6.0 g of freshly distilled methyllithium chloride in 10 mL of THF (40 °C), and work up by procedure B to yield 5.5 g of crude product. Distillation *in vacuo* provides 3.9 g (37%) of pure 2-methyl-5-phenylhex-1-ene (3d) (bp 65 °C/0.1 mm): ¹H NMR (500 MHz) 7.20–7.00 (m, 5H), 4.75 (d, 1H, *J* = 0.5), 4.71 (d, 1H), 2.53 (m, 1H, *J* = 7.0, 7.0), 1.94 (m, 1H, *J* = 20), 1.90 (m, 1H), 1.67 (m, 1H), 1.61 (m, 1H), 1.57 (s, 3H), 1.14 (d, 3H); ¹³C NMR (125.8 MHz) 148.18, 146.11, 129.15, 127.76, 126.70, 110.74, 40.47, 37.26,

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36.71, 22.93; IR 3100–2800, 1649, 1604, 1494, 886, 761, 700; UV 260 (2.31), 202 (3.94); GC-MS 174 (5) [M⁺], 159 (8) [M⁺ – CH₃], 118 (100) [C₉H₁₀⁺], 105 (70) [C₈H₉⁺], 91 (25) [C₇H₇⁺].

2-Methyl-5-phenyl-hex-2-ene (3b). Compound **3d** (0.5 g) is added to 10 mL of a 0.1 M solution of potassium *tert*-butoxide in HMPT and stirred under argon in a Schlenk flask for 2 days at 50 °C. The deep purple solution is quenched with saturated NH₄Cl (150 mL) and extracted with hexanes (4 50-mL portions). The extract is washed with 100 mL of brine and 100 mL of water, dried over anhydrous K₂CO₃, filtered, and concentrated. Vacuum distillation affords 0.45 g (90%) of an 8:92 mixture of **3d** and **3b**: ¹H NMR (300 MHz) 7.25–7.00 (m, 5H), 5.14 (tm, 1H, *J* = 7.6, 7.0), 2.64 (m, 1H, *J* = 7.0, 7.0, 7.0), 2.30 (dd, 1H), 2.20 (dd, 1H), 1.59 (s, 3H), 1.45 (s, 3H), 1.18 (d, 3H); ¹³C NMR (125.8 MHz) 148.21, 132.46, 129.03, 127.80, 126.63, 124.03, 41.24, 37.80, 26.21, 22.06, 18.23; IR 3100–2800, 1603, 1494, 759, 699; GC-MS 174 (8) [M⁺], 105 (100) [C₈H₉⁺], 91 (6) [C₇H₇⁺]; UV 260 (2.34), 202 (4.13) (corrected for the absorbance of **3d**).

2-Phenyl-5-methylhex-1-ene (3c). (a) A 1-L flask fitted with an efficient condenser and a stirring bar is charged with 94.4 g (0.8 mol) of freshly distilled α -methylstyrene, 90 g (0.5 mol) of *N*-bromosuccinimide (NBS), and 50 mL of freshly distilled CCl₄. The reaction mixture is heated to 130–140 °C; finally at 180 °C spontaneous, vigorous boiling begins. The exothermic reaction is moderated by intermittent cooling in an ice/water bath until all of the NBS is dissolved and reaction ceases. Cooling to room temperature precipitates succinimide, which is removed by filtration. The mother liquor is distilled *in vacuo* (0.1 mm): first to remove solvent and excess α -methylstyrene (25–70 °C) and then to give 68 g (69%) of a colorless oil consisting of 3-bromo-2-phenylprop-1-ene and 1-bromo-2-phenylprop-1-ene in the ratio 63:37 (GC).

(b) Following the general procedure, a Grignard reagent is prepared from 8.4 g of isobutyl bromide and treated with the 63:37 mixture of 8.0 g of bromides above in 10 mL of THF. Removal of solvent *in vacuo* affords a mixture of **3c** and 1-bromo-2-phenylprop-1-ene, which is added in 5 mL of THF to a mixture of 5 g of Mg turnings in 25 mL of THF and 0.3 mL of 1,2-dibromoethane. Stirring for 2 h, quenching with aqueous NH₄Cl, and extraction with hexanes provides α -methylstyrene and 2-phenyl-5-methylhex-1-ene (**3c**), distillation of which *in vacuo* affords 2.2 g of pure **3c** as a colorless liquid: bp 65 °C/0.1 mm; ¹H NMR (500 MHz) 7.33 (d, 2H), 7.15 (t, 2H), 7.08 (t, 1H), 5.28 (d, 1H, *J* = 1.7), 5.04 (dd, 1H, *J* = 1.4), 2.43 (dt, 2H, *J* = 7.9), 1.46 (m, 1H, *J* = 6.6), 1.27–1.37 (m, 2H), 0.81 (d, 6H); ¹³C NMR (125.8 MHz) 149.4, 141.94, 128.53, 127.51, 126.47, 112.06, 37.90, 33.68, 28.07, 22.65; IR 3100–2800, 1627, 1600, 1494, 893, 777, 703; UV 240 (3.97), 206 (4.19); GC-MS 174(8) [M⁺], 131 (15) [M⁺ – C₃H₇], 118 (100) [C₉H₁₀⁺], 91 (15) [C₇H₇⁺].

(E)- and (Z)-2-Methyl-5-phenylhex-3-ene (3e(E) and 3e(Z)). A Wittig reaction (*vide supra*) between 27 g of isobutyltriphenylphosphonium bromide⁵¹ in 150 mL of THF and 5.5 g of 2-phenylpropionaldehyde (Aldrich Chemical Co.) in 25 mL of THF affords, after distillation (bp 65 °C/0.1 mm), 6.4 g (90%) of **3e(E)** and **3e(Z)** in the ratio 12:88: GC-MS (of the mixture) 174 (15) [M⁺], 131 (100) [M⁺ – C₃H₇], 118 (85) [C₉H₁₀⁺], 105 (90) [C₈H₉⁺], 91 (65) [C₇H₇⁺]. The NMR spectra can be distinguished by virtue of the large difference in relative intensities. **3e(E)**: ¹H NMR (300 MHz) 7.30–7.00 (td, 5H), 5.57 (m, 1H, *J* = 15.4), 5.41 (m, 1H), 3.33 (m, 1H, *J* = 6.9), 2.19 (m, 1H, *J* = 6.7), 1.28 (d, 3H), 0.93 (d, 6H). **3e(Z)**: ¹H NMR (300 MHz) 7.25–7.00 (td, 5H), 5.40 (td, 1H, *J* = 10.1), 5.17 (td, 1H), 3.69 (dq, 1H, *J* = 7.0, 9.5), 2.61 (dsept, 1H, *J* = 6.6, 9.6), 1.25 (d, 3H), 0.94 (d, 3H), 0.84 (d, 3H).

Series 4.⁵² **4-(2',4'-Dimethylphenyl)but-1-ene (4c).** To a solution of allyl magnesium bromide from allyl bromide (30.5 g) in ether at 0 °C is added dropwise, 2,4-dimethylbenzyl chloride⁵⁷ (38.8 g). After 6 h (slow warming to 25 °C), the reaction is worked up by shaking with

saturated aqueous NH₄Cl, decantation, and distillation to give a mixture of 4-(2',4'-dimethylphenyl)but-1-ene and starting chloride. The latter is removed by refluxing over Mg in ether and hydrolyzing with saturated aqueous NH₄Cl. Distillation affords **4c**: 5.0 g; bp 92–94 °C/10 mm; IR 3090, 995, 910; UV 291.5 (3.20), 302.0 (2.95).

(E)-1-(2',4'-Dimethylphenyl)but-1-ene (4a(E)). Compound **4c** (0.3 M) is isomerized on a preparative scale with NaOEt (0.5 M) in HMPT at 90 °C for 1 h. Separation by preparative GC (column C) affords (*E*)-1-(2',4'-dimethylphenyl)but-1-ene (**4a(E)**) as the major component (UV 291.5 (3.20), 302.0 (2.95); IR 1380, 1620, 960, 845) and (*Z*)-1-(2',4'-dimethylphenyl)but-1-ene (**4a(Z)**) as the first minor eluent (UV, broad of weaker intensity than that of **4a(E)**; IR 1615, 1405, 830). The second minor eluent is (*E*)-1-(2',4'-dimethylphenyl)but-2-ene (**4b(E)**):⁵³ UV 276.6 (2.53); IR 1620, 1380, 960.

Series 5. (E)-1-Mesitylbut-1-ene (5a(E)). A stirred solution of the reaction mixture from *n*-propylmagnesium bromide and mesityl-aldehyde⁵⁴ (1-mesitylbutan-1-ol, 25 g, 0.13 mol) in 100 mL of anhydrous ether is treated with phosphorus tribromide (11.0 g, 0.04 mol) in a cooled (<0 °C) 500-mL, 3-necked flask bearing a reflux condenser, mechanical stirrer, addition funnel, and drying tube. After the addition, the solution is warmed to 25 °C, boiled under reflux for 2 h, and left standing for 12 h. Addition of ice and water and extraction with ether (50 mL) gives an ethereal extract, which is washed successively with 5% aqueous NaHCO₃, 5% H₂SO₄, and ice water, and dried (MgSO₄). Distillation affords a slightly red material, which is dissolved in ether, washed with dilute aqueous NaOH, dried, and redistilled to give colorless **5a(E)** (13.3 g (60%); bp 108–109 °C/17 mm; lit. bp 90–100 °C/12 mm;⁵³ 114 °C/21 mm;⁵⁵ 110 °C/20 mm⁵⁶). IR 970 cm⁻¹, (lit. 968⁵³). The olefinic coupling constant (*J* = 16.5 Hz) confirms the trans structure.

4-Mesitylbut-1-ene (5c). An ethereal solution of chloromethyl-mesitylene⁵⁷ (5.0 g) is added dropwise to allyl magnesium bromide in diethyl ether (from 4.0 g of allyl bromide). Stirred and boiled under reflux for 6 h and washed with saturated aqueous NH₄Cl, the reaction mixture affords 4-mesitylbut-1-ene (2.25 g) after distillation, as shown by the infrared and NMR spectra.

Series 6. (E)-2-(2',4'-Dimethylphenyl)pent-3-ene (6b(E)). Dropwise addition of α,γ -dimethylallyl bromide⁵⁸ (15.0 g) in ether to the Grignard reagent from 2,4-dimethylbromobenzene (15.0 g) and magnesium turnings (2.4 g, 0.10 g-atom), boiling under reflux for 3 h, and the usual workup gives **6b(E)** (38%; bp 101–102 °C/10 mm). All GC columns tested indicate a single compound; NMR and IR at 970 cm⁻¹ indicate the trans, unconjugated structure.

Series 7. (E)- and (Z)-2-(2',6'-Dimethylphenyl)pent-3-ene (7b(E) and 7b(Z)). A Grignard reagent in THF from 2,6-dimethylbromobenzene (10.0 g) is treated dropwise with α,γ -dimethylallyl bromide (9.0 g). The resulting mixture is stirred and heated at 60 °C for 12 h, cooled, and treated with saturated aqueous NH₄Cl. The light yellow THF layer is decanted, washed with dilute NaOH, dried over Mg₂SO₄, and distilled to yield 3.6 g of **7b(E)** and **7b(Z)** (bp 77–79 °C/2.5 mm).

Series 8. (E)- and (Z)-2-Mesitylbut-3-ene (8b(E) and 8b(Z)). Both stereoisomers have been prepared and characterized by Goering et al.⁵⁹ Following the procedure above, mesityl magnesium bromide and α,γ -dimethylallyl bromide yield 1.0 g (0.0053 mol) of a colorless liquid (bp 115–118 °C/5 mm). The major product is (*E*)-2-mesitylbut-3-ene (**8b(E)**), about 10% of which is **8b(Z)** and a small amount is (*E*)-1-mesitylbut-2-ene.

(E)- and (Z)-2-Mesitylbut-2-ene (8a(E) and 8a(Z)). The mixture of **8b(E)** and **8b(Z)** above is completely rearranged in KOC(CH₃)₃/HMPT at 90 °C under kinetic control to **8a(E)**, the ratio to **8a(Z)** being

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80.4 to 10.6, whereas after 120 h, equilibrium is established, the ratio becoming 22:75 in favor of **8a(Z)**.

Equilibrations. Purification of HMPT. In Series 1–3, the system for effecting the equilibrations consists of hexamethylphosphoric triamide (HMPT) as solvent and freshly sublimed potassium *tert*-butoxide (KO-*t*-Bu), strictly free of *tert*-butyl alcohol, as strongly basic catalyst.⁶⁰ An effort to remove the water, a serious poison of the catalyst, from the various commercially available samples of HMPT by distillation from CaH₂ proves inadequate. Stirring for 2 days at 80 °C over LiAlH₄ or heating with a small amount of *n*-butyllithium (2.5 M in hexane solution) at 100 °C for 3 h, followed by distillation *in vacuo*, only a middle cut being taken, provides HMPT, which now is anhydrous below the limits of detection. Another worry involves the possibility of the highly reactive, proton-containing pentamethylphosphoric triamide (PMPT) being one of several impurities detectable by GC and NMR. A variable peak in the range 2–4 ppm is removed after extraction with D₂O but reappears upon addition of traces of H₂O. Even after thorough drying and distillation, two peaks (δ 2.52 and 2.45) remain. Although the HMPT is ~99.7% of purity, three impurities are revealed by GC (column DB-1): retention times 20.37 (HMPT, 21.13), 24.01, and 27.22 min. Purification by multiple crystallization of the neat solvent removes all but one of the impurities (24.01 min). After ten recrystallizations, HMPT of >99.9% of purity is obtained. Coinjection of a synthetic sample of PMPT⁶¹ shows it is not an impurity. In summary, recrystallization of meticulously dried HMPT and use of sublimed KO-*t*-Bu lead to a catalytic system more active by a factor of ~10 than a catalyst similarly prepared from dry but not recrystallized HMPT.

The upper temperature is limited in the present instance by the wish to stay with a single preparation of one catalyst system and not to reduce catalytic activity to achieve higher useful temperatures by the addition, for example, of *tert*-butyl alcohol. In one variation, sealed, prescored ampules (Wheaton, 1 mL, borosilicate glass) are stored in triethylamine, dried > 12 h at 150 °C, evacuated, baked with a heat-gun, cooled, and flushed with argon. These are loaded with a standard solution, sealed and heated at the desired temperature for the specified length of time. This procedure is generally quite convenient, but positions of equilibrium are not reproducible at the highest temperatures because cooling cannot be accomplished fast enough to preclude significant displacement of equilibrium during the process. Kinetically more rapid interconversions are particularly susceptible (e.g., **3a(E)** and **3b(E)**). In a second procedure, equilibrations are conducted in *rubber-sealed*, Pyrex tubes (350 × 4 mm) so that the catalyst can be quenched *prior* to cooling by the injection of 1 mL of water.

Procedure. A standard 0.1 M solution is prepared by pumping HMPT under argon pressure into a flask containing the requisite amount of KO-*t*-Bu, dissolved by magnetic stirring and used at once. The mixture for equilibration is prepared by introducing into a large ampule, by means of gas-tight syringes, ~100 μ L of the starting olefin, ~10 μ L of bicyclohexyl as standard, and ~2.5 mL of the 0.1 M catalyst solution.

In the first procedure, aliquots are distributed among 5 ampules at –78 °C, one being quenched immediately with 1 mL of water and analyzed as described below to fix a standard for determining the percent recovery in the other ampules after heating. The remaining ampules are then sealed *in vacuo* and placed in the appropriate constant-temperature environment. Progress toward equilibrium is monitored by analyzing ampules at appropriate intervals. Ampules are quickly cooled by immersion into a vigorously stirred bath of isopropyl alcohol/dry ice before opening, after which the contents are quenched by the addition of 1 mL of water and extracted with 1 mL of hexanes. After being washed thrice with 1-mL portions of water and passed through filter paper, the solution is analyzed directly.

When rubber-sealed tubes are used at ambient pressure, they are first pretreated as described above. The standard solution is prepared as above in one of the ampules and then distributed under argon in equal portions into four tubes, a small amount being reserved for quenching and analysis to serve as reference. Rubber septa are taped to the tubes, and the reaction vessels are kept at the specified

temperature for the various periods of time. Quenching is effected prior to cooling with 1 mL of water. Thereafter, the same procedure as above is followed.

Analysis. Samples (0.8–1.2 μ L) of the hexane solutions of the olefins are injected into the gas chromatograph and their areas are recorded. The mean of 3–4 injections is determined with a precision of about 3% of the concentration of the individual component expressed as percent of the sum. Response factors are obtained for GC-purified samples of the pure olefins (>99%) relative to the most stable isomer ($f = 1$). The differences were small, the largest being 0.10 (**3a(E)** and **3d**) and 0.031 (**2a(Z)** and **2b**). Concentrations are corrected by the response factors and reported as ratios of concentrations to the sum of all the isomeric olefins, $\ln(c_i/\sum c_{i-j})$, in the Supporting Information as Tables S1, S2, and S3.

Retention Times (in min) (Relative Response Factors). Phenylbutenes [column DB-1701; initial T , 60 °C; final T , 125 °C; rate, 3°/min]: 4-Phenylbut-1-ene (**1c**) 11.67; 1-phenylbutane, 11.85; (*E*)-1-phenylbut-2-ene (**1b(E)**), 12.66; (*Z*)-1-phenylbut-1-ene (**1a(Z)**), 13.07; (*Z*)-1-phenylbut-2-ene (**1b(Z)**), 13.38; 1-methylindane, 13.50; (*E*)-1-phenylbut-1-ene (**1a(E)**), 15.66; bicyclohexyl, 21.55; (1-methylind-1-ene, 17.05; not present). Phenylpentenes [column DB-1; initial T , 80 °C; final T , 150 °C; rate 4°/min; final time, 40 min]: (*Z*)-1-phenyl-3-methylbut-1-ene (**2a(Z)**), 14.06 (0.991); 1-phenyl-3-methylbutane, 14.69; 4-phenyl-2-methylbut-1-ene (**2c**), 15.04 (1.012); 1-phenyl-3-methylbut-2-ene (**2b**), 16.14 (1.022); (*E*)-1-phenyl-3-methylbut-1-ene (**2a(E)**), 16.56 (1.000, st); bicyclohexyl, 22.11. Phenylheptenes [column DB-1; initial T , 80 °C; final T , 250 °C; rate 4°/min; final time, 30 min]: (*Z*)-2-phenyl-5-methylhex-3-ene, 19.02; (*Z*)-2-phenyl-5-methylhex-2-ene, (**3a(Z)**), 19.29 (0.969); (*E*)-2-phenyl-5-methylhex-3-ene, 19.72; 2-methyl-5-phenylhexane, 19.86; 2-methyl-5-phenylhex-1-ene (**3d**), 20.68 (0.934); 2-methyl-5-phenylhex-2-ene (**3b**), 20.98 (1.000); 5-methyl-2-phenylhex-1-ene (**3c**), 21.28 (1.034); bicyclohexyl, 22.11; (*E*)-5-methyl-2-phenylhex-2-ene (**3a(E)**), 23.15 (1.000, st).

Calculations. Linear regression analysis (Microsoft program EXCEL, version 4.0) of the function $\ln(c_i/\sum c_{i-j}) = -\Delta H^\circ/RT + \Delta S^\circ/R$, gives values of “ ΔH° ” directly from the slope and “ ΔS° ” from the intercept. Differences are $\Delta\Delta H$ (in kcal/mol) and $\Delta\Delta S$ (in eu (cal mol⁻¹ K⁻¹)). This method of handling the data gives an unambiguous measure of the standard error of each individual component. Corresponding values for the differences in Gibbs free energy are derived by the usual equation, from which equilibrium constants for any pair can also be calculated.

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Supporting Information Available: Thermochemical data on which Figure 1 is based, data relating to equilibrations at various temperatures for series **1**, **2**, and **3** and their plots (Figures 2–4), and Figure 5 showing chemical shifts of hydrogens in styrenes and compounds **8a(E)** and **8a(Z)** (13 pages). See any current masthead page for ordering and Internet access instructions.

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