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Table S1. Heats of Hydrogenation from Pedley et al.⁵ and D. W. Rogers²⁰ of Monosubstituted Ethenes

	$\Delta_f H^\circ$ (Pedley) ^a	ΔH_{H_2} (Pedley) ^b	ΔH_{H_2} (Rogers) ^c	Steric Energy ^d	ΔH_{H_2} (SEcorr) ^e	
Propene	+4.78			+0.25		
		-29.80			-31.05	
Propane	-25.02			+1.50		
1-Butene	0.00			+1.48		
		-30.02			-30.71	
<i>n</i> -Butane	-30.02			+2.17		
1-Pentene	-5.09			+1.48		
		-30.02			-30.69	
<i>n</i> -Pentane	-35.11			+2.82		
3-MeButene-1	-6.60			+2.49		
		-30.14			-31.28	
2-MeButane1	-36.74			+3.63		
Hexene-1	-10.40			+2.80		
		-29.54	-30.28		[-30.95]	
<i>n</i> -Hexane	-39.94			+3.47		
3-MePentene-1	-11.83			+4.50		
		(-29.30)	-29.78		[-30.80]	
3-MePentane	-41.13			+5.52		
4-MePentene-1	-12.26			+3.47		
		-29.52	-30.28		[-31.11]	
4-MePentane	-41.78			+4.30		
3,3-DiMeButene-1	-14.46			+3.29		
		-30.02	-30.07		-31.74	
2,2-DiMeButane	-44.48			+5.01		
Heptene-1	-14.90			+3.44		
		-29.96	-29.92		-30.63	
<i>n</i> -Heptane	-44.86			+4.11		

3-MeHexene-1	[−15.96]			+4.74		
			−29.76		[−31.23]	
3-MeHexane	−45.72			+6.21		
			(−29.33)		[−30.22]	
4-MeHexene-1	[−16.39]			+5.32		
5-MeHexene-1	−15.70			+4.23		
		−29.91	−29.76		−30.60	
2-MeHexane	−45.61			+4.92		
4,4-DiMePentene-1	−19.50			+4.22		
		−29.71			−31.20	
4,4-DiMePentane	−49.21			+5.71		
		−29.81 ± 0.26 (11) ^f	−29.90 ± 0.32 (8) ^g		−30.94 ± 0.39 (13)^h	
		−29.91 ± 0.22 (17)ⁱ				

^a Heats of formation from Pedley et al.⁵ ^b Derived heats of hydrogenation. Values in parenthesis are excluded from the grand mean (in bold face). ^c Heats of hydrogenation from Rogers.²⁰

^d Steric energies (SE) as produced by the Allinger MM2 program contained in CSC Chem 3D Pro™.

^e Heats of hydrogenation derived by subtraction of SE values from Pedley values or

Rogers values [in brackets]. ^f Mean of all values from Pedley et al.⁵ ^g Mean of all Rogers'

values.²⁰ ^h Mean of all SE-corrected values. ⁱ Mean of all values not excluded in parentheses.

Table S2. Heats of Hydrogenation from Pedley et al.⁵ and D. W. Rogers²⁰ of 1,1-Disubstituted Ethenes

	$\Delta_f H^\circ$ (Pedley)	ΔH_{H_2} (Pedley)	ΔH_{H_2} (Rogers)	Steric Energy	ΔH_{H_2} (SE corr)	
2-MePropene	-4.04			-0.03		
		-28.03			-30.00	
2-MePropane	-32.07			+1.94		
2-MeButene-1	-8.44			+1.84		
		-28.30			-30.09	
2-MeButane	-36.74			+3.63		
2-MePentene-1	[-13.98]			+2.50		
		-27.58	-27.80		[-29.60]	
2-MePentane	-41.78			+4.30		
2,3-DiMeButene-1	[-14.81]			+3.70		
		-27.65	-27.80		[-29.89]	
2,3-DiMeButane	-42.61			+5.79		
2,4-DiMePentene-1	-20.05			+3.20		
		-28.20			-30.62	
2,4-DiMePentane	-48.25			+5.62		
2-EtButene-1	-13.38			+3.82		
		-27.75	-27.68		-29.45	
3-MePentane	-41.13			+5.52		
2-MeHexene-1	[-17.93]			+3.12		
			-27.68		[-29.48]	
2-MeHexane	-45.61			+4.92		
2-Et-3-MeButene-1	-19.00			+6.12		
		(-28.54)			-30.61	
2,3-DiMePentane	-47.54			+8.19		
2,3,3-TriMeButene-1	-20.43			+6.47		
		-28.45			-30.24	
2,2,3-TriMeButane	-48.88			+8.26		
		-28.06 ± 0.37 (8)	-27.74 ± 0.07 (4)		-30.00 ± 0.44 (9)	
		-27.90 ± 0.30 (11)				

Table S3. Heats of Hydrogenation from Pedley et al.,⁵ D. W. Rogers²⁰ and K. B. Wiberg²¹ of *trans*-1,2-Disubstituted Ethenes

	$\Delta_f H^\circ$ (Pedley)	ΔH_{H_2} (Pedley)	ΔH_{H_2} (Rogers)	Steric Energy	ΔH_{H_2} (SEcorr)	$\Delta_f H^\circ$ (KBW) (hydration)
<i>trans</i> -Butene	-2.72			+0.14		
		-27.30			-29.33	
<i>n</i> -Butane	-30.02			+2.17		
<i>trans</i> -Pentene	-7.62			+1.34		-7.68
		-27.49			-28.97	-27.43
<i>n</i> -Pentane	-35.11			+2.82		
<i>trans</i> -Hexene-2	-12.88			+2.01		-13.00
		-27.06	-27.45		-28.91	-26.94
<i>n</i> -Hexane	-39.94			+3.47		
		-26.94	(-28.18)		-29.14	-27.20
<i>trans</i> -Hexene-3	-13.00			+2.51		-12.74
<i>trans</i> -4-Me-Pentene-2	-14.70			+2.31		
		-27.08	-27.29		-29.07	
2-Me-Pentane	-41.78			+4.30		
<i>trans</i> -4,4-DiMe-Pentene2	-21.22			+4.04		
		(-27.99)			-29.66	
2,2-DiMe-Pentane	-49.21			+5.71		
<i>trans</i> -Heptene-2	[-17.59]			+2.64		-17.56
			-27.27		-28.74	-27.30
<i>n</i> -Heptane	-44.86			+4.11		
			-27.41		-28.34	-27.40
<i>trans</i> -Heptene-3	[-17.45]			+3.18		-17.46
<i>trans</i> -4-Me-Hexene-2	[-19.14]			+3.75		
			(-26.58)		-29.04	
3-Me-Hexane	-45.72			+6.21		
<i>trans</i> -5-Me-Hexene-2	[-18.75]			+2.77		
			-26.86		-29.01	
2-Me-Hexane	-45.61			+4.92		
			-27.56		-29.02	
<i>trans</i> -2-Me-Hexene-3	[-18.05]			+3.46		
			-27.31 ± 0.39 (6)	-27.20 ± 0.33 (8)	-29.02 ± 0.33 (11)	-27.25 ± 0.20 (5)
					-27.25 ± 0.21 (16)	

Table S4. Heats of Hydrogenation from Pedley et al.,⁵ D. W. Rogers²⁰ and K. B. Wiberg²¹ of *cis*-1,2-Disubstituted Ethenes

	$\Delta_f H^\circ$ (Pedley)	ΔH_{H_2} (Pedley)	ΔH_{H_2} (Rogers)	Steric energy	ΔH_{H_2} (SEcorr)	$\Delta_f H^\circ$ (KBW) (hydration)
<i>cis</i> -Butene	-1.70			+1.55		
		-28.32			-28.94	
<i>n</i> -Butane	-30.02			+2.17		
<i>cis</i> -Pentene	-6.60			+2.66		-6.75
		-28.51	-28.56		-28.67	-28.36
<i>n</i> -Pentane	-35.11			+2.82		
<i>cis</i> -Hexene-2	[-11.38]			+3.22		-12.26
		(-27.44)	-28.56		[-28.80]	(-27.68)
<i>n</i> -Hexane	-39.94			+3.47		
		-28.56	(-29.06)		-28.42	-28.17
<i>cis</i> -Hexene-3	-11.38			+3.61		-11.77
<i>cis</i> -4-Me-Pentene-2	-13.74			+3.31		
		-28.04	-27.94		-29.03	
2-Me-Pentane	-41.78			+4.30		
<i>cis</i> -4,4-DiMe-Pentene-2	-17.32			+9.15		
		(-31.49)			-28.45	
2,2-DiMe-Pentane	-49.21			+5.71		
<i>cis</i> -Heptene-2	[-17.23]			+3.86		-16.51
			(-27.63)		(-27.88)	-28.35
<i>n</i> -Heptane	-44.86			+4.11		
			-28.32		-28.24	-28.34
<i>cis</i> -Heptene-3	[-16.54]			+4.19		-16.52
<i>cis</i> -4-Me-Hexene-2	[-18.06]			+6.06		
			(-27.63)		(-27.78)	
3-Me-Hexane	-45.72			+6.21		
<i>cis</i> -5-Me-Hexene-2	[-17.81]			+3.92		
			-27.80		-28.80	
2-Me-Hexane	-45.61			+4.92		
			-28.27		-28.83	
<i>cis</i> -2-Me-Hexene-3	[-17.34]			+4.36		
		-28.73 ± 1.41 (6)	-28.20 ± 0.49 (9)		-28.61 ± 0.36 (10)	-28.21 ± 0.27 (6)
				-28.29 ± 0.23 (14)		

Table S5. Heats of Hydrogenation from Pedley et al.⁵ and D. W. Rogers²⁰ of 1,1,2-Trisubstituted Ethenes

	$\Delta_f H^\circ$ (Pedley)	ΔH_{H_2} (Pedley)	ΔH_{H_2} (Rogers)	Steric Energy	ΔH_{H_2} (SE corr)	
2-MeButene-2	-9.99			+1.72		
		-26.75			-28.66	
2-MeButane	-36.74			+3.63		
2-MePentene-2	[-15.11]			+2.64		
		(-25.79)	-26.67		[-28.33]	
2-MePentane	-41.78			+4.30		
(E)-3-MePentene-2	-15.08			+3.66		
		-26.05			-27.91	
3-MePentane	-41.13			+5.52		
		-26.24			-28.58	
(Z)-3-MePentene-2	-14.89			+3.18		
2-MeHexene-2	[-19.61]			+3.22		
			-26.00		-27.70	
2-MeHexane	-45.61			+4.92		
(Z)-3-MeHexene-2	[-20.05]			+3.73		
			-25.67		-28.15	
3-MeHexane	-45.72			+6.21		
(Z)-3-MeHexene-3	[-19.57]			+4.51		
		(-27.36)	-26.15		[-27.85]	
3-MeHexane	-45.72			+6.21		
		-26.74	-26.43		-28.82	
(E)-3-MeHexene-3	-18.98			+4.13		
2,4-DiMePentene-2	-21.20			+5.26		
		-27.05			-27.41	
2,4-DiMePentane	-48.25			+5.62		
		-26.57 ± 0.56 (7)	-26.18 ± 0.39 (5)		-28.15 ± 0.47 (9)	
		-26.38 ± 0.43 (10)				

Supplnft Series 1: Data from Equilibrations at Various Temperatures given as Natural Logarithms of the Ratios of Concentrations of Individual Isomers to the Sum of All Concentrations in % (Temperature in Kelvin)

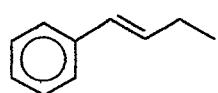
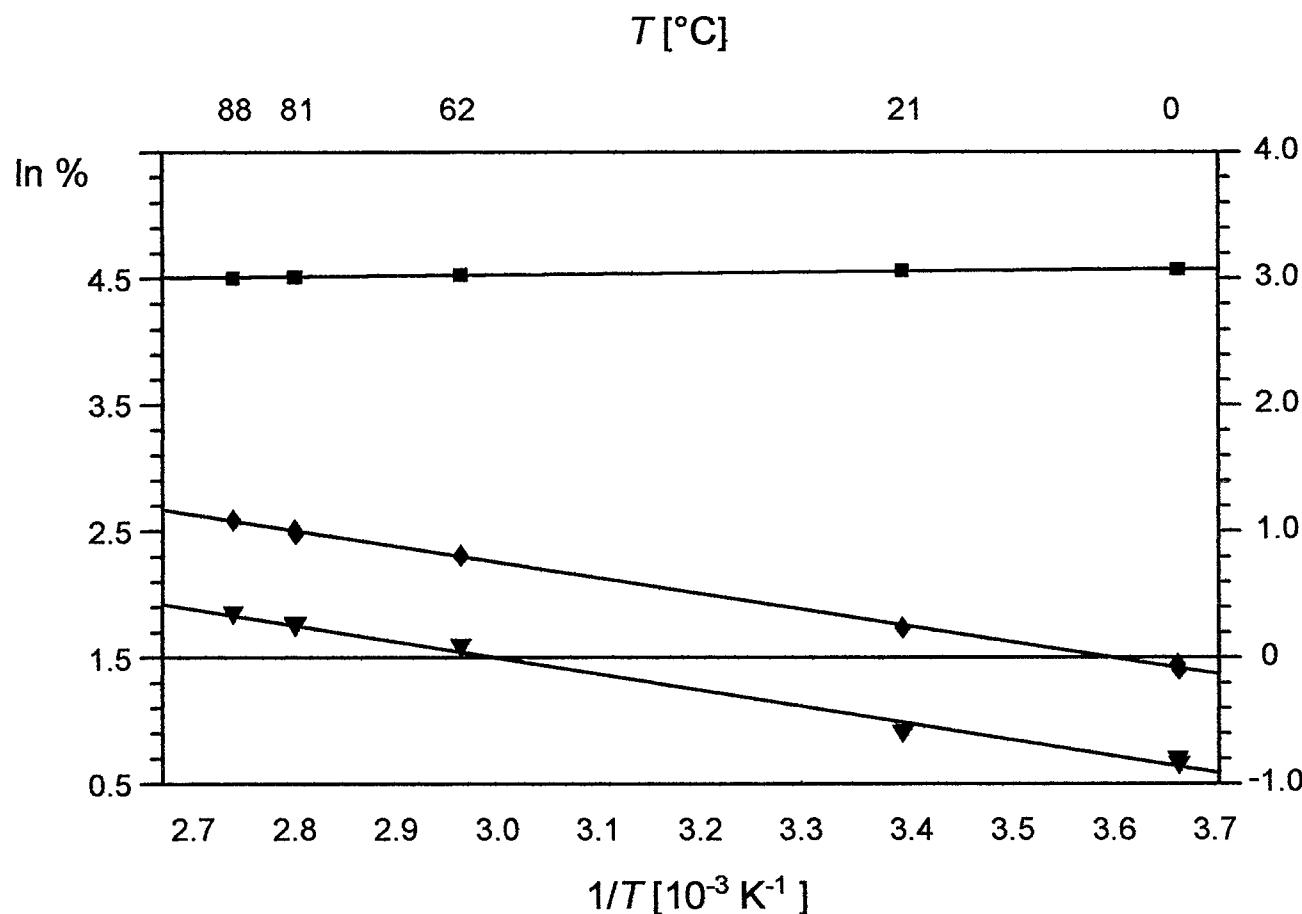
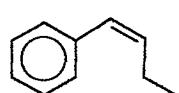
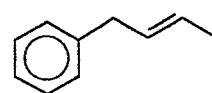
T(K)	$K^{-1} \times 10^3$	1a(E)	1b(E)	1a(Z)	1b(Z)
Series 1: 1-Phenyl-butenes: KO<i>t</i>-Bu/HMPT					
273.2	3.661	4.576	0.647	-0.094	
273.2	3.661	4.575	0.688	-0.051	
294.2	3.400	4.567	0.896	0.239	
335.4	2.982	4.532	1.581	0.811	
354.0	2.825		1.753	0.982	
354.0	2.825	4.517	1.747	1.008	
361.4	2.767	4.508	1.841	1.089	
Series 1: 1-Phenyl-butenes: RuH/C₆H₆					
334.7	2.988	4.508	1.701	0.828	0.392
335.2	2.984	4.508	1.701	0.842	0.365
354.2	2.824	4.489	1.883	0.993	0.548
353.7	2.828	4.486	1.866	1.026	0.673
371.1	2.695	4.469	2.026	1.109	0.742
370.2	2.702	4.468	1.993	1.154	0.829
384.2	2.603	4.448	2.105	1.286	1.008
384.4	2.602	4.442	2.123	1.356	1.026

SupplInf Table Series 2. Data from Equilibrations at Various Temperatures given as Natural Logarithms of the Ratios of Concentrations of Individual Isomers to the Sum of All Concentrations in % (Temperature in Kelvin)

$T(K)$	$K^{-1} \times 10^3$	2a(<i>E</i>)	2 b	2a(<i>Z</i>)	2c
Series 2: 1-Phenyl-3-methyl-butenes: KO<i>t</i>-Bu/HMPT					
273.2	3.661	4.317	3.148	-0.830	0.611
291.2	3.428	4.259	3.289	-0.743	0.940
334.1	2.994	4.134	3.510	-0.337	1.440
334.1	2.994	4.137	3.508	-0.270	1.391
353.8	2.827	4.080	3.579	-0.104	1.597
370.2	2.702	4.033	3.623	0.005	1.797
370.3	2.701	4.038	3.625	-0.039	1.740

Supplnfo Table Series 3. Data from Equilibrations at Various Temperatures given as Natural Logarithms of the Ratios of Concentrations of Individual Isomers to the Sum of All Concentrations in % (Temperature in Kelvin)

T(K)	$K^{-1} \times 10^3$	3a(E)	3 b	3a(Z)	3 c	3 d
Series 3: 2-Phenyl-5-methyl-hexenes: KO<i>t</i>-Bu/HMPT						
354.0	2.825	4.065	3.183	2.482	0.997	0.918
360.2	2.777	4.056	3.195	2.477	1.038	0.979
370.9	2.697	4.032	3.212	2.516	1.102	1.070
381.7	2.620	4.015	3.239	2.507	1.162	1.144
383.2	2.610	4.010	3.240	2.520	1.152	1.176
384.3	2.603	4.009	3.237	2.527	1.158	1.176
384.2	2.603	4.002	3.243	2.540	1.181	1.170
391.3	2.556	3.989	3.255	2.545	1.221	1.235
405.2	2.468	3.962	3.260	2.576		1.282
426.9	2.343	3.926	3.305	2.588	1.397	1.427

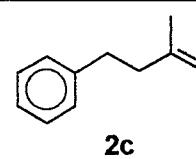
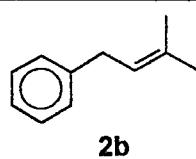
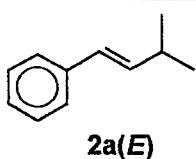
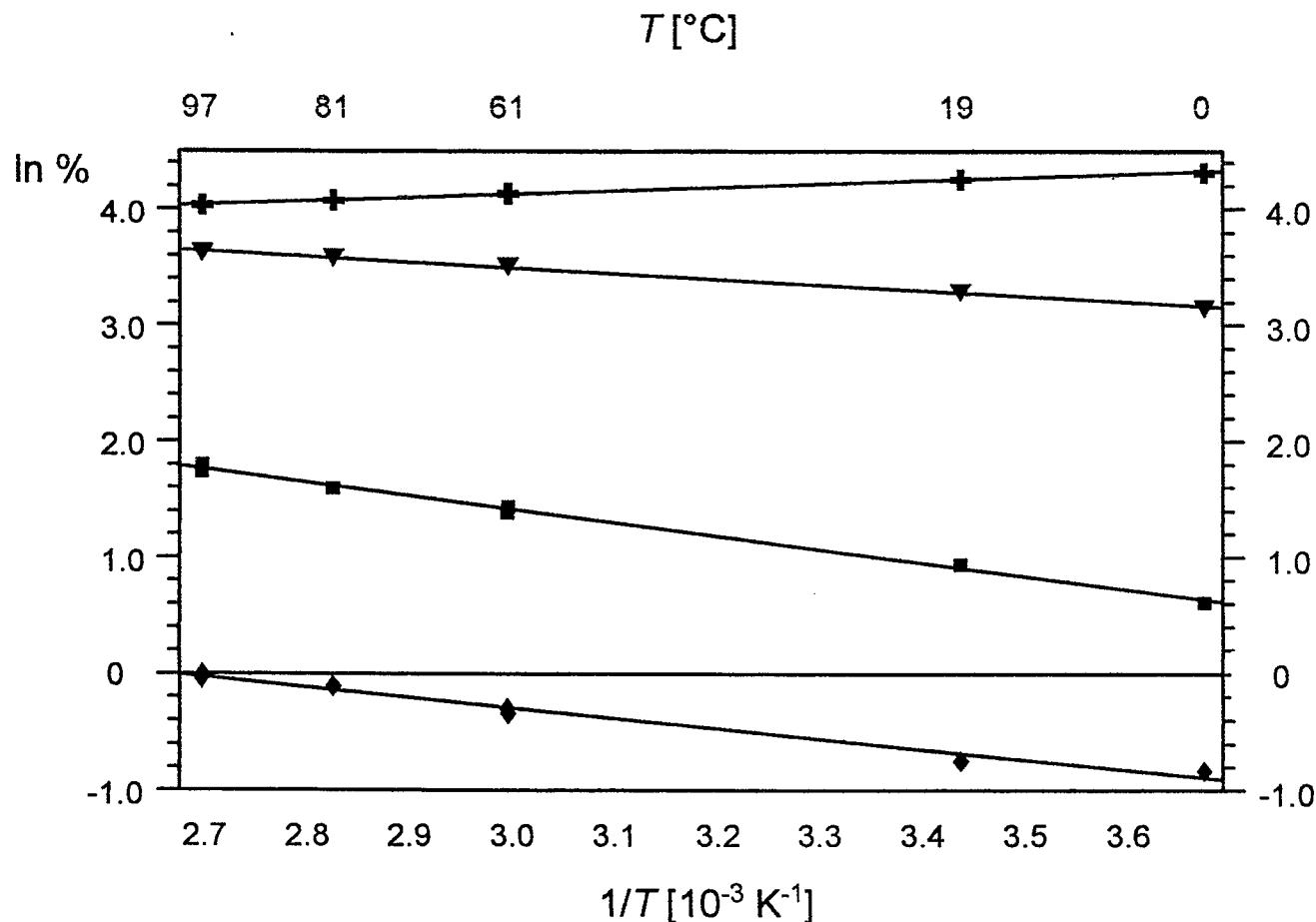
**1a(*E*)****1a(*Z*)****1b(*E*)**

“ΔH” -0.15 ± 0.01 2.57 ± 0.04 2.65 ± 0.10

“ΔS” 8.56 ± 0.03 9.26 ± 0.13 10.98 ± 0.32

SupInfo Figure 2 for Scheme 1. The natural logarithm of the quotient of the concentration at equilibrium of one isomer and the sum of all isomers (ln%) is plotted against $10^3 K^{-1}$ for the series 1 of β -ethylstyrenes: **1a(*E*)**, ■; **1a(*Z*)**, ◆, **1b(*E*)**, ▼.

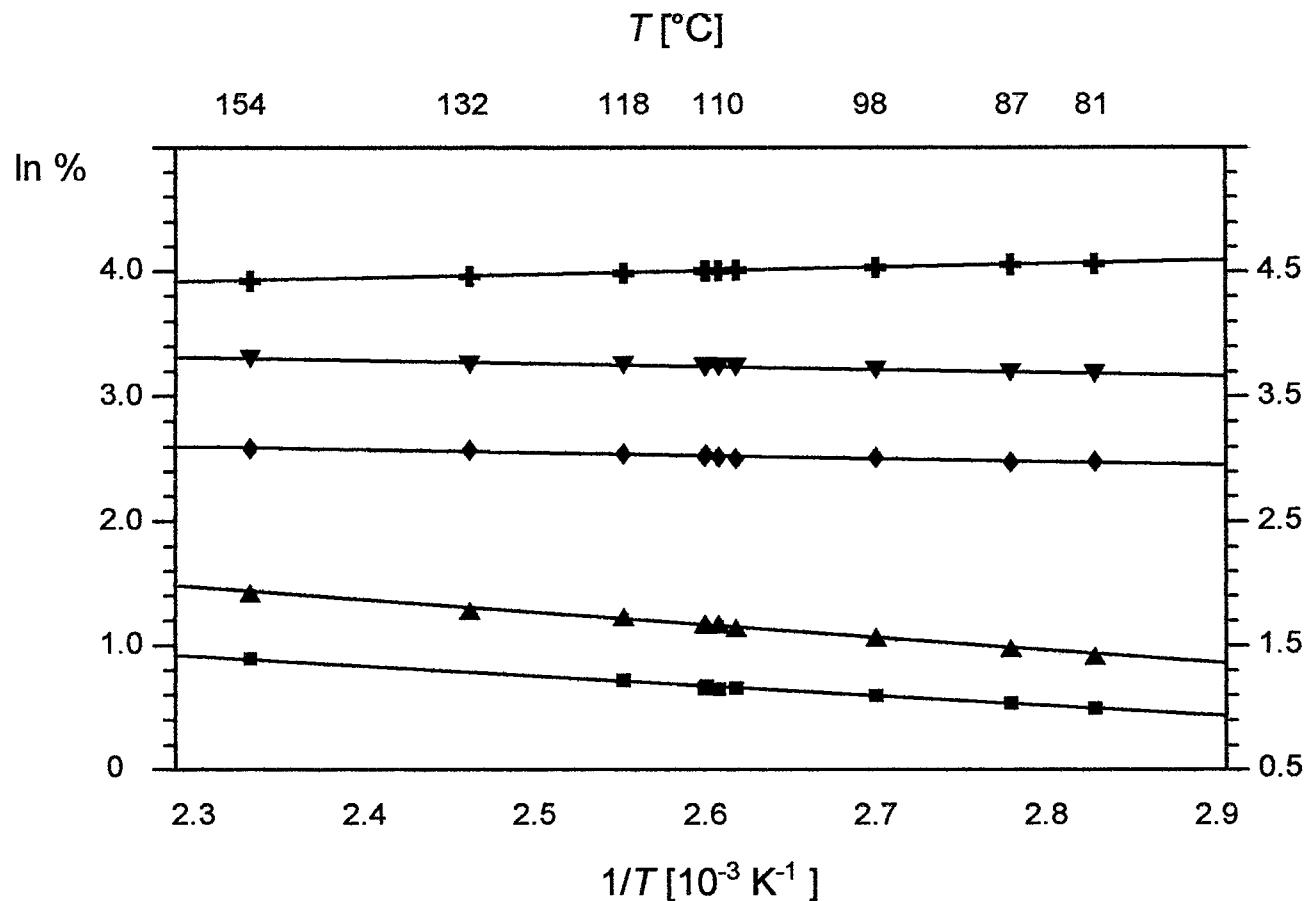
Differences between any pair of “ΔH” are $\Delta\Delta_f H$ in kcal/mol and any pair of “ΔS” are $\Delta\Delta_f S$ in $\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, these latter values being shown in Chart 1, Series 1.



ΔH^*	-0.59 ± 0.02	0.98 ± 0.03	2.34 ± 0.07	1.78 ± 0.11
ΔS^*	6.45 ± 0.05	9.87 ± 0.10	9.83 ± 0.21	4.75 ± 0.33

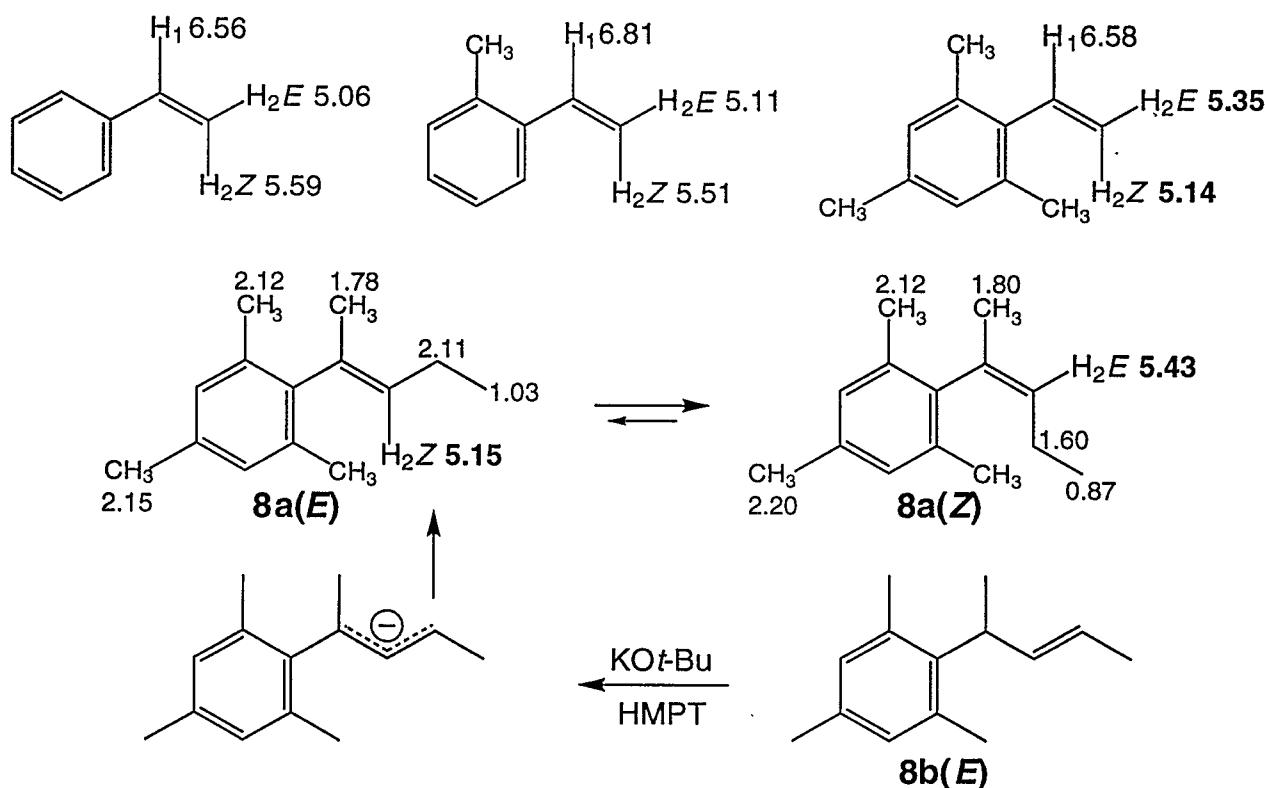
SuplInfo Figure 3 for Scheme 2. The natural logarithm of the quotient of the concentration at equilibrium of one isomer and the sum of all isomers ($\ln\%$) is plotted against 10^3 K^{-1} for the series 2 of β -isopropylstyrenes: **2a(*E*)**, +; **2b**, ▼; **2c**, ■; **2a(*Z*)**, ◆.

◆. Differences between any pair of " ΔH^* " are $\Delta\Delta_f H$ in kcal/mol and any pair of " ΔS^* " are $\Delta\Delta_f S$ in $\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, these latter values being shown in Chart 1, Series 2.



	$3a(E)$	$3b$	$3a(Z)$	$3d$	$3c$
ΔH°	-0.59 ± 0.02	0.49 ± 0.03	0.49 ± 0.05	2.07 ± 0.07	1.64 ± 0.05
ΔS°	6.43 ± 0.04	7.70 ± 0.07	6.30 ± 0.14	7.69 ± 0.19	6.60 ± 0.14

SuplInfo Figure 4 for Scheme 3. The natural logarithm of the quotient of the concentration at equilibrium of one isomer and the sum of all isomers ($\ln\%$) is plotted against $10^3 K^{-1}$ for the series 3 of β -ethylstyrenes: $3a(E)$, +; $3b$, \blacktriangledown ; $3a(Z)$, \blacklozenge ; $3d$, \blacktriangle ; $3c$, \blacksquare . Differences between any pair of " ΔH° " are $\Delta\Delta_f H$ in kcal/mol and any pair of " ΔS° " are $\Delta\Delta_f S$ in $\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; these latter values are shown in Chart 1, Series 3.

Figure 5

SupInfo Figure 5. NMR chemical shifts of the vinyl hydrogen atoms in styrene, o -methyl and 2',4',6'-trimethylstyrene emphasize the change in order of the β -hydrogen atoms. Isomerization of $8b(E)$, catalysed by potassium *t*-butoxide in hexamethylphosphoric triamide and interrupted before equilibration, affords $8a(E)$ as the major product, but, after equilibration, $8a(Z)$ appears as the more stable isomer. The values of NMR chemical shifts are shown. Methyl groups in the mesityl moiety and at the α -position are unaffected by configuration, whereas hydrogens of the ethyl groups are. In one isomer, vinyl hydrogen is at higher field while its congeneric methylene and methyl groups are at lower field, whereas in the second, the reverse is true. Based on the strong presumption that the ortho methyl groups at 2' and 6' have forced the olefinic group toward an orthogonal orientation and that some groups then occupy space closer to the Karplus cone, the (*Z*) configuration is assigned to the first isomer, (*E*) to the second. These assignments accord with the expectation that kinetically controlled isomerization of $8b(E)$ generates the less hindered anionic intermediate shown and thus favors $8a(E)$, whereas at equilibrium $8a(Z)$ is the major product.