toward hydrolysis makes the use of the latter compound undesirable. We have developed a simpler and nontoxic method employing 5-piperidinomethylene Meldrum's acid, which itself is readily obtained in a one-pot reaction[14] between Meldrum's acid, piperidine, and triethyl orthoformate.

Dry ether (9 mL) was added to magnesium turnings (1.08 g, 45 mmol) in a three-necked flask under N_2. Methyl iodide (6.39 g, 45 mmol) dissolved in 5 mL of dry ether was added slowly with stirring. After the reaction had subsided, 2,2-dimethyl-5-(1-piperidinylmethylene)-1,3-dioxane-4,6-dione[14] (8.36 g, 35 mmol) dissolved in 100 mL of dry tetrahydrofuran was added in the course of 20 min, and the resulting mixture was stirred for a further 30 min and then poured into 200 mL of 2 N HCl. Extraction with methylene chloride (4 × 100 mL), drying over $MgSO_4$, filtering, and evaporation of the solvent gave a yellowish oil, which was "sublimed" at 30 °C (10^{-4} Torr) to furnish 5.47 g (92%) of **1b**: mp 58–59 °C (lit.[13] mp 58.5–60 °C); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 8.02 (q, J = 7.5 Hz, 1 H), 2.48 (d, J = 7.5 Hz, 3 H), 1.73 (s, 6 H); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 163.6 (d, C-H vinyl), 161.7 (s, CO), 159.8 (s, CO), 119.2 (s, C-5), 104.8 (s, C-2), 27.7 (q, $(CH_3)_2$), 17.7 (q, CH_3).

Trapping of Carboxy(vinyl)ketene 14 with Methanol. **1b** (100 mg, 0.588 mmol) was pyrolyzed at 400 °C in the preparative apparatus and the product trapped with methanol on the cold finger (see under Apparatus). Excess methanol was distilled in vacuum and the product dried in high vacuum and subjected to NMR analysis: yield 79 mg (94%) of a 1:1 mixture of (*Z*)- and (*E*)-methyl 2-ethylidenemalonate (**16**, **17**). **16**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.79 (s, 1 H, COOH), 7.66 (q, J = 7.4 Hz, 1 H), 3.88 (s, 3 H, OCH_3), 2.31 (d, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 172.4 (s, CO), 166.6 (s, CO), 154.7 (dq, ^1J = 157.4 Hz, ^3J = 6.9 Hz, C-3 vinyl), 124.4 (br s, C-2), 52.8 (q, ^1J = 148.3 Hz, OCH_3), 16.5 (qd, ^1J = 128.9 Hz, ^3J = 1.9 Hz, CH_3). **17**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.74 (s, 1 H, COOH), 7.69 (q, J = 7.4 Hz, 1 H), 3.85 (s, 3 H, OCH_3), 2.12 (d, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 167.1 (s, CO), 166.3 (s, CO), 151.7 (dq, ^1J = 159.2 Hz, ^3J = 7.0 Hz, C-3 vinyl), 126.3 (br s, C-2), 52.4 (q, ^1J = 148.3 Hz, OCH_3), 16.2 (qd, ^1J = 29.0 Hz, ^3J = 2.6 Hz, CH_3); mass spectrum (field desorption) *m/z* 145 ($[M + 1]^+$, 100%).

Trapping of Ethylideneketene (15) to (*E*)-Crotonanilide (20). 2,2-Dimethyl-5-ethylidene-1,3-dioxane-4,6-dione (**1b**; 100 mg, 0.588 mmol) was pyrolyzed at 600 °C in the preparative apparatus, and the products were trapped with aniline on the cold finger as described above. After the end of the experiment, excess aniline was removed in high vacuum and the product taken up in chloroform and washed three times with 30 mL of 1.5 N HCl and then three times with 30 mL of H_2O. After drying, removal of the solvent in vacuum, and further drying in high vacuum, the white solid residue (77.6 mg, 82%) was identified as (*E*)-crotonanilide (**20**) by IR and ^{1}H NMR comparison with an authentic sample, prepared[15] from (*E*)-crotonyl chloride and aniline and itself verified by IR[16] and ^{1}H NMR spectroscopy. A trace of the *Z* isomer was apparent in the sample of **20** obtained from **15**, but none of the 3-butenoic anilide (**21**). Use of longer contact times (higher pressure) or higher pyrolysis temperature resulted in the formation of **21** as already reported.[7] **20**: ^{1}H NMR ($CDCl_3$, 90 MHz) δ 8.05 (br s, 1 H, NH), 7.66–6.72 (m, 6 H, C_6H_5 + H(C-2)), 5.98 (dq, $^3J_{2,3}$ = 15.0 Hz, $^3J_{3,4}$ = 1.5 Hz, 1 H, H(C-3)), 1.81 (dd, $^3J_{2,4}$ = 6.6 Hz, $^3J_{3,4}$ = 1.5 Hz, 3 H, CH_3).

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Thermochemistry of the "Orthogonal" Butadienes (*Z*,*Z*)-3,4-Dimethylhexa-2,4-diene and 2,3-Di-*tert*-butylbuta-1,3-diene

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Abstract: The "orthogonal" dienes of the title, (*Z*,*Z*)-**1** and **6**, having the planes of their double bonds at a dihedral angle not far from 90°, serve as models for "conjugated" dienes lacking π-electron delocalization and for the transition state for interconversion of antiperiplanar (trans) and synperiplanar (cis or gauche) butadiene. Several effects on properties attributable to their nonplanar conformations are recorded. Structures are assigned to (*Z*)-3-methyl-4-methylenehex-2-ene ((*Z*)-**2**) and (*Z*)- and (*E*)-3,4-dimethylhexa-1,3-diene ((*Z*)-**3**, (*E*)-**3**) by application of the 1,5-dienyl hydrogen shift. The thermochemistries of (*E*,*E*)-**1**, (*E*,*Z*)-**1**, and (*Z*,*Z*)-**1**, the isomers of 3,4-dimethylhexa-2,4-diene (**1**), and of 2,3-di-*tert*-butylbutadiene (**6**) are established by base-catalyzed equilibration and catalytic hydrogenation. Discrepancies between experimental and modeled enthalpies of formation accord with the operation of planarity-demanding, π-electron delocalization.

An enduring interest in butadiene and its family of conjugated dienes has focused on the torsional energy profile, i.e., on change in enthalpy as the dihedral angle between planes of the two double bonds is varied from 0° (trans) to 180° (cis).[1,2] At the experimental and theoretical levels, most recently advanced (and reviewed) by Mui and Grunwald[1b] and Breulet, Lee, and Schaeffer,[2a] respectively, there is now general agreement that the antiperiplanar, trans conformation, long accepted as the global minimum, is separated by a transition state, higher by some 6–7 kcal/mol at a dihedral angle of 80–85°, from a gauche (<180°) or cis (180°) conformation, lying some 2.3–2.5 kcal/mol above trans.[1b,c,2a] The question of whether gauche or cis is the local minimum, if still unresolved, looks to be answered in favor of cis,[1a] or, if gauche, by a very small barrier of ~0.1 kcal/mol.[1c,2a]

At the time the work at Yale was started more than two decades ago, the existence of a trans–cis barrier had not been demonstrated

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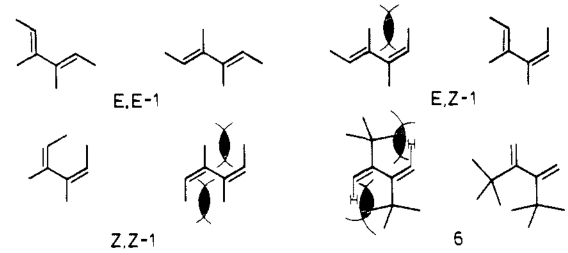

Figure 1. 3,4-Dimethylhexa-2,4-dienes (*E,E*)-**1**, (*E,Z*)-**1**, and (*Z,Z*)-**1** and 2,3-di-*tert*-butylbuta-1,3-diene (**6**) shown in cis (180°) and trans (0°) conformations.

and Dewar and Schmeising[3] had recently proposed that sp^2–sp^2 hybridization of the single bond joining the double bonds might be the origin of the resonance energy of butadiene rather than π-electron delocalization, as defined in the classical work of Kistiakowsky.[4] To distinguish the angular *independent*, hybridization hypothesis[3] from the angular *dependent*, π-delocalization hypothesis,[5] in which stabilization is greatest at 0° and null at 90°, thermochemical examination of dienes having dihedral angles fixed at or near 90° seemed reasonable. In the event, establishment of a 6–7 kcal/mol barrier to the torsional interconversion of *trans*- and *cis*-butadiene[1] removed doubts about π-electron delocalization being the origin of the minima.

It is the present purpose to determine the thermochemistry of nonplanar dienes (Figure 1) whose conformations have been sterically forced far from coplanarity to dihedral angles now known through analysis by electron diffraction. These data, it is hoped, will serve in the development of a molecular and/or quantum mechanical program for conjugated dienes.

We begin with observations on 3,4-dimethylhexa-2,4-dienes and their tautomers, proceed to clarify thermochemistry by base-catalyzed equilibration and catalytic hydrogenation, and conclude with an attempted analysis of the implications for the origin of conjugative interaction in dienes.

Three 3,4-Dimethylhexa-2,4-dienes (*E,E*)-1, (*E,Z*)-1, and (*Z,Z*)-1. The first two of these dienes were prepared in 1959 by Criegee and Noll,[6] who correctly assigned their structures on the basis of the failure of (*E,Z*)-**1** to absorb in the ultraviolet. Although (*Z,Z*)-**1** had been isolated at Yale from the mixture of dienes obtained by acid- or alumina-catalyzed dehydration at 500 °C of the 3,4-dimethylhexane-3,4-diols,[7] its preparation in quantity was more convenient following the procedure of Denny and Davis,[8] in which the lithium derivative of (*Z*)-2-bromo-2-butene was coupled by means of cobaltous chloride. Showing no ultraviolet absorption in the conventional region (≥200 nm), (*Z,Z*)-**1** was assigned an essentially "orthogonal" conformation by Denny and Davis.[8]

Professor Traetteberg of the University of Trondheim generously agreed to establish the configuration and conformation of the three dienes **1** by electron diffraction.[9] Noteworthy were the dihedral angles of 113–114° (cis taken as 180°) between the two planes containing the double bonds in (*E,Z*)-**1** and (*Z,Z*)-**1** and the essential invariance of the C_3–C_4 bond length at 147 ± 1 pm (Table I) in all three isomers regardless of dihedral angle. Inferences about conformation based on UV spectra, including those of Reeve and Reichel,[10] were consistent with Traetteberg's (1970) results,[9] but a dihedral angle of 90° was clearly not an energy minimum in (*E,Z*)-**1** and (*Z,Z*)-**1**.

Table I. Physical Properties of the 3,4-Dimethylhexa-2,4-dienes

property	(*E,E*)-**1**	(*E,Z*)-**1**	(*Z,Z*)-**1**
bp, °C	134.5	113.5	102.5
$n^{20}{}_D$	1.4758	1.4397	1.4299
$d^{20}{}_4$	0.7922	0.7516	0.7293
R	39.2	38.6	39.0
$r(C_1—C_2)^a$	152	152	153
$r(C_2═C_3)^a$	135	135	136
$r(C_3—C_4)^a$	147	148	146
α_1,[b] deg	26.6	114.3	113.3
$\lambda_{max}{}^c$	224	171	168

[a] Bond distances from Traetteberg in picometers.[9] [b] Dihedral angles, from Traetteberg,[9] between the planes, C_2,C_3,C_3 CH_3 and C_5,C_4,C_4 CH_3 (trans conformation defined as 0°). [c] Wavelength in nanometers; data of Professor V. Vaida.[11]

Table II. ^1H and ^{13}C NMR Spectra of the 1,2,3,4-Tetramethylbutadienes

group[a]	(*E,E*)-**1**	(*E,Z*)-**1**	(*Z,Z*)-**1**
	^1H NMR (270 MHz, $CDCl_3$)[b,c]		
C_1 CH_3	1.71 (d, *J* 6.6)	1.56 (dq, *J* 6.6, 1.3)	1.45 (dq, *J* 6.6, 1.3)
C_4 CH_3		1.65 (d, *J* 6.9)	
C_2 CH_3	1.76 (s)	1.66 (s)	1.71 (dq, *J* 1.3, 1.4)
C_3 CH_3		1.73 (dq, *J* 1.3)	
$C_{1(4)}$ H	5.58 (q, *J* 6.6)	5.20 (m)	5.26 (qq, *J* 6.6, 1.4)
	^{13}C NMR (67.8 MHz, $CDCl_3$)		
$C_{2(3)}$	137.1 (0.21)[d]	140.7 (0.15) 135.8 (0.12)	136.6 (0.21)
$C_{1(4)}$	119.1 (1.00)	121.1 (0.83) 118.9 (1.00)	119.6 (0.52)
$C_{2(3)}$ CH_3		23.3 (1.00)	22.1 (1.00)
	14.0 (0.62)	15.1 (0.47)	
$C_{1(4)}$ CH_3		14.5 (0.66)	14.1 (0.67)
	13.5 (0.75)	13.3 (0.48)	

[a] Numbering based on butadiene for convenience. [b] Ppm relative to TMS. [c] Splittings (*J*) in hertz. [d] Values in parentheses are relative intensities.

From the ^1H NMR spectra (reported here because of additional information provided by higher resolution; cf. ref 10) and the ^{13}C NMR spectra reported in Table II, it is immediately apparent which isomer has the nonsymmetrical, (*E,Z*) configuration.

Two features in the ^1H spectra are distinctive: rotation of an (*E*) double bond out of the plane shifts the vinyl proton from 5.58 ppm in (*E,E*)-**1** to 5.20 ppm in (*E,Z*)-**1**; replacement of a (*Z*) double bond in nonplanar (*Z,Z*)-**1** by an (*E*) double bond in nonplanar (*E,Z*)-**1** causes the (*Z*)-C_1 CH_3 group to be shifted downfield from 1.45 to 1.56 ppm.

In the ^{13}C spectra, assignment of $C_{1(4)}$ and $C_{2(3)}$ rests not only on the greater intensity of the former but also on multiplicities found with the INEPT pulse sequence. (*E*)- and (*Z*)-methyl are distinguished in $C_{2(3)}$ CH_3.

Despite identical values of α_1 found by electron diffraction in (*E,Z*)-**1** and (*Z,Z*)-**1**, only the latter fails to react with sulfur dioxide[10] or maleic anhydride.[7] Apparently, the second α,δ-dimethyl repulsion in (*Z,Z*)-**1** makes attainment of a planar cis conformation sufficiently less favorable that the transition state for a Diels–Alder reaction is no longer within reach.

Spectra extending into the vacuum ultraviolet have been measured in the gas phase[11] and are interpreted with reference

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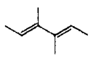
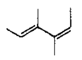
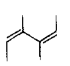
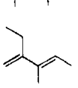
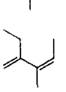
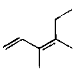
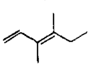
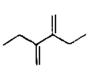
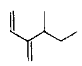
(10) Reeve, W.; Reichel, D. M. *J. Org. Chem.* **1972**, *37*, 68–72.

(11) Professor V. Vaida, unpublished results. UV and VUV spectra are obtained with a 1-m spectrometer (Acton Research Corp.). The spectroscopic samples are used at ~1 Torr in a 10-cm cell. The gas-phase spectra of the three olefins follow (frequency in nanometers, intensities relative to that of the strongest absorption in percent): (*E,E*)-**1**: 230.9, 56; 223.7, 100; 216.0, 32 (sh); 209.1, 31; 202.2, 19; 198.3, 13; 194.9, 11. The first three features are assigned to vibrational structure of the B_{1u} valence excited, electronic state; the following bands are part of the Rydberg series extending into the VUV. (*E,Z*)-**1**: 196, 13 (sh); 191, 17 (sh); 185, 25 (sh); 175, 68; 171, 100. (*Z,Z*)-**1**: 195, 2 (sh); 185, 9 (sh); 171, 69; 168, 100. Previously reported spectra[10] of (*E,Z*)-**1** and (*Z,Z*)-**1** should now be considered obsolete and to have been artifacts of instrumentation.

Table III. Equilibrium Concentrations and GC Relative Retention Times of Isomeric Conjugated Dienes of the 3,4-Dimethylhexyl Skeleton

isomer		RRT[a]	ΔΔ*G*[b]	*i*/(*E*,*E*)-**1**[c]
	(*E*,*E*)-**1**	1.00 (1.00)	0.000	(1.000)
	(*E*,*Z*)-**1**	0.33 (0.37)	1.07	0.227
	(*Z*,*Z*)-**1**	0.24 (0.28)	1.14	0.207
	(*E*)-**2**	0.65 (0.61)	1.44	0.137
	(*Z*)-**2**	0.29 (0.31)	2.89	0.018
	(*Z*)-**3**	0.83	2.16	0.050
	(*E*)-**3**	0.91	2.33	0.039
	**4**	0.58 (0.42)	4.22	0.003
	**5**			

[a] Relative retention times (RRT) on Carbowax column B (see the Experimental Section); those of Reeve and Reichel[10] in parentheses. [b] In kilocalories/mole. [c] Fraction of isomer *i* relative to (*E*,*E*)-**1** at equilibrium in hexamethylphosphoric amide at 90 °C (see Table VI).

to molecules containing conjugated and unconjugated olefinic bonds. Vibrational analysis of the UV spectra of ethene,[12] butadiene,[13] hexatriene,[13] and octatetraene[12] have yielded equilibrium geometries for the excited electronic states with respect to the ground state. Whereas these spectra indicate that the excited B_u state (λ_{max} ~165 nm) of ethylene is twisted by ~90°,[12] all molecules with conjugated double bonds[13] exhibit intense, structured UV spectra (transition origins: 216 nm, butadiene; 251 nm, hexatriene; 281 nm, octatetraene) that indicate planar, excited-state structures upon Frank–Condon analysis.

Within this framework, the UV spectra for (*E*,*Z*)-**1** and (*Z*,*Z*)-**1** (λ_{max} 171 and 168 nm, respectively) are interpreted as transitions from nonplanar, ground states to highly twisted excited states. In contrast, (*E*,*E*)-**1** exhibits an intense, structured band (λ_{max} 224 nm) consistent with a transition in which ground-state planarity is preserved in the excited, B_u state.

Photoelectron spectra of (*E*,*E*)-**1**, (*E*,*Z*)-**1**, (*Z*,*Z*)-**1**, and **6** have been determined by Heilbronner et al.[14] and compared with those of several dienes of known antiplanar conformation. Analysis indicates dihedral angles of approximately 0, 110, 105, and 105°, respectively, that agree well with the electron diffraction angles (Table I). The inference of a 90° structure drawn from molecular models of **6** is well confirmed.

The remarkable range of boiling points of the three configurational isomers, previously noted by Reeve and Reichel,[10] has stimulated the determination of their indices of refraction and densities. The result is a good correlation between lower boiling point and lower density. Deviation from planarity in (*E*,*Z*)-**1** and (*Z*,*Z*)-**1** looks the factor responsible for the lowered density. The derived molar refractivities of all three isomers, however, show the positive increment classically associated with 1,3-dienes, despite the considerable twisting out of the plane. The calculated value of *R* (38.2) may be compared with the experimental values given in Table I.

Table IV. Thermochemistry of 3,4-Dimethylhexa-2,4-dienes (**1**) and 2,3-Di-*tert*-butyl-1,3-butadiene (**6**)

property	(*E*,*E*)-**1**	(*E*,*Z*)-**1**	(*Z*,*Z*)-**1**	**6**
exptl ΔΔ*G*(90 °C, l)	0.00	+1.07	+1.14	
symm cor[a]	0.00	+0.50	0.00	
cor ΔΔ*G*(90 °C, l)	0.00	+1.57	+1.14	
exptl ΔH_H[b]	-49.98	-52.20	-51.05	-57.74
cor $\Delta\Delta H_s$[c]	+0.20	+0.20	+0.20	+0.20
cor $\Delta\Delta H_V°$[d]	-0.82	+0.12	+0.63	+0.69
cor $\Delta H_H°$(g)	-50.60	-51.88	-50.22	-56.85
$\Delta H_f°$(alkane, g)	-51.14[e]	-51.14[e]	-51.14[e]	-73.82[f]
$\Delta H_f°$(dienes, g)	-0.54	+0.74	-0.92	-16.97

[a] Symmetry numbers of (*E*,*E*)-**1**, (*E*,*Z*)-**1**, and (*Z*,*Z*)-**1** are 2, 1, and 2, respectively; at 90 °C, *RT* ln 2 = 0.50 kcal/mol. [b] Experimental heats of hydrogenation in isooctane in kilocalories/mole. [c] Correction for the double-bond increment to heats of solution differences in isooctane (see Table VIII). [d] Correction for estimated heats of vaporization differences (see Table IX). [e] Heat of formation of a 60:40 mixture of *rac*- and *meso*-3,4-dimethylhexane calculated by MM2.[5] [f] Heat of formation of *rac*-2,3-di-*tert*-butyl-1,3-butane calculated by MM2.[5]

Table V. Thermal Rearrangements of (*E*,*Z*)-**1**, (*Z*,*Z*)-**1**, and (*Z*)-**3**[a]

	compn,[b,c] %		
T, s^{-1}	(*E*,*Z*)-**1**	(*Z*)-**3**	(*Z*,*Z*)-**1**
0	99.83	0.17	0.00
1 800	97.91[d]	2.00	0.09
3 000	97.63	2.27	0.10
3 600	96.48	3.35	0.17
8 700	94.08	5.52	0.40
9 000	93.12	6.40	0.48
10 800	92.30[d]	6.80	0.90
18 000	91.61	7.27	1.12
19 200	90.31	7.82	1.87
21 600	89.48[d]	8.35	2.17
43 200	84.27[d]	10.05	5.68
86 400	77.99	9.29	12.72
172 800	68.93	8.71	22.36
345 600	58.62	8.04	33.34
0	0.00	0.00	100.00
1 200	0.07	0.29	99.64
2 400	0.08	0.53	99.39
3 600	0.13	0.76	99.11
7 200	0.40	1.30	98.30
10 800	0.78	1.69	97.54
21 600	2.31	2.41	95.28
86 400	12.89	3.85	83.26
172 800	23.48	4.51	72.01
259 200	28.44	5.13	66.43
777 600	42.68	6.42	50.90
0	0.34	99.48	0.18
1 200	8.37	89.12	2.51
2 400	15.37	80.45	4.18
3 600	22.02	71.70	6.28
7 200	37.07	53.59	9.54
10 800	47.73	39.82	12.45
21 600	62.98	19.87	17.15

[a] Heated in vapors above boiling tetralin (207.8 ± 0.2 °C). [b] Normalized to 100%. [c] Average of three GC injections. [d] Mean of two runs.

Other Conjugated Dienes of the 3,4-Dimethylhexyl Skeleton. Equilibration among eight of the nine possible conjugated dienes derived from the 3,4-dimethylhexane skeleton can be effected under the strongly basic conditions discovered by Schriesheim et al.[15] (realized here by 0.1 M potassium *tert*-butoxide in hexamethylphosphoric amide, HMPA). These isomers, shown in Table III along with their GC relative retention times, have been characterized by Reeve and Reichel,[10] with the exception of (*E*)-**3**, (*Z*)-**3**, and **5**.

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Table VI. Base-Catalyzed[a] Rearrangement of (*E*,*E*)-**1** and (*Z*,*Z*)-**1**

t, s	(*Z*,*Z*)-**1**[b]	(*Z*)-**2**	(*E*,*Z*)-**1**	**4**	(*E*)-**2**	**3**[c]	(*E*,*E*)-**1**
2160[d]	0.0031	0.0120	0.1484	0.0018	0.0921	0.0757	0.6670
3900	0.0086	0.0121	0.1539	0.0017	0.0938	0.0592	0.6706
5700	0.0130	0.0125	0.1406	0.0017	0.0909	0.0541	0.6690
7570	0.0208	0.0124	0.1534	0.0022	0.0893	0.0597	0.6622
9300	0.0250	0.0117	0.1512	0.0022	0.0907	0.0557	0.6634
2220[e]	0.9614		0.0152		0.0016		0.0217
3660	0.9243		0.0199		0.0057		0.0502
5400	0.8755		0.0291		0.0124		0.0810
7260	0.8513		0.0315		0.0134		0.1038

[a] Hexamethylphosphoric amide, 0.1 M potassium *tert*-butoxide at 90 °C. [b] Concentrations are fractions of total recovered dienes, normalized to 100%. [c] The ratio of (*E*)-**3** to (*Z*)-**3** is 1.27 in this mixture. [d] (*E*,*E*)-**1** is the starting diene. [e] (*Z*,*Z*)-**1** is the starting diene.

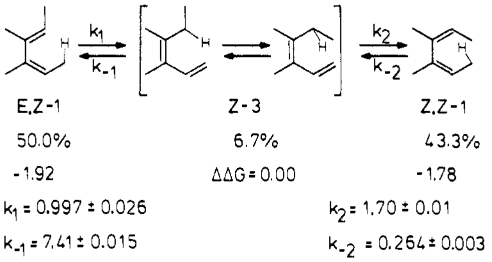

Figure 2. System of (*E*,*Z*)-**1**, (*Z*,*Z*)-**1**, and (*Z*)-**3** equilibrated at 207.8 ± 0.2 °C by thermal 1,5-dienyl hydrogen shift. Equilibrium concentrations (%), $\Delta\Delta G$ (kcal/mol, relative to (*Z*)-**3**), and first-order, specific rate constants (10^{-5} s^{-1}) are derived from the data in Table V.

Advantage is taken of the established stereochemistry of the concerted 1,5-dienyl hydrogen migration[16] to assign configurations to (*Z*)-**3** and (*E*)-**3**. As outlined in Figure 2, (*Z*)-**3**, having its ethyl group cis to the vinyl group, may equilibrate thermally with two members of the **1** series and is indeed the essential intermediate in the thermal interconversion of (*E*,*Z*)-**1** and (*Z*,*Z*)-**1**. Among the other isomers in Table III, (*Z*)-**2** and (*E*)-**3** are also interconvertible by intramolecular 1,5-dienyl hydrogen shift.

From the experimental data (Table V) on the rearrangements of (*E*,*Z*)-**1**, (*Z*,*Z*)-**1**, and (*Z*)-**3** at 207.8 ± 0.2 °C, values for first-order, specific rate constants have been calculated by a SIMPLEX program for optimization of numerical solutions of the set of three differential equations implied in Figure 2. Despite marked departure from planarity and trivial difference in free energy ($\Delta\Delta G$ = 0.14 kcal/mol; cf. 0.07 kcal/mol in HMPA at 90 °C), (*E*,*Z*)-**1** and (*Z*,*Z*)-**1** rearrange at rates comparable with that of (*E*,*Z*)-2-deuterio-6-methylocta-2,4-diene ($k = 0.7 \times 10^{-5}$ s^{-1} at 207.5 °C).[16] Parenthetically, the discrepancy in the differences between gas-phase and solution free energies of (*E*,*Z*)-**1** and (*Z*)-**3** is larger ($\Delta\Delta G$ = 1.92 versus 1.09 in HMPA at 90 °C).

After being heated at 208 °C for 24 h or longer, (*Z*)-**2** is set into equilibrium with a single product, (*E*)-**3**: $K_{208\,°C}$((*Z*)-**2**/(*E*)-**3**) = 1.27 ± 0.01 ($\Delta\Delta G_{208\,°C}$ = 230 cal/mol; cf. 560 cal/mol in HMPA at 90 °C).

Free Energy Differences among the Isomeric Dienes. In preliminary kinetic experiments on the base-catalyzed rearrangement of the C_8H_{14} dienes of this paper, all isomers except (*Z*,*Z*)-**1** had reached equilibrium after 1 h at 55 °C. This observation allowed the analysis of the kinetics of the appearance and disappearance of (*Z*,*Z*)-**1** to be simplified by the assumption of a pseudo-first-order, reversible model in which the other isomers are treated collectively as a set of "products" in preequilibrium. A glance at the data from (*E*,*E*)-**1** in Table VI furnishes justification for this approach.

$$\text{"products"} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (Z,Z)\text{-}\mathbf{1}$$

At 90.0 ± 0.2 °C in HMPA, 0.1 M in potassium *tert*-butoxide, equilibrium among *all* isomers is established after 120 h. From many independent runs starting with (*E*,*E*)-**1**, (*E*,*Z*)-**1**, (*Z*,*Z*)-**1**, or (*E*)-**2**, the ratio of (*Z*,*Z*)-**1** to (*E*,*E*)-**1** at equilibrium is 0.207, corresponding to a fraction of (*Z*,*Z*)-**1** among all isomers of 0.123. The equilibrium data (starting from (*E*,*E*)-**1** or (*Z*,*Z*)-**1**) are collected in Table III as ratios and $\Delta\Delta G$ relative to (*E*,*E*)-**1**.

The order of stability runs parallel to the degree of alkyl substitution; that is, tetrasubstituted isomers are highest and monosubstituted, the undetected **5**, lowest. The estimated $\Delta\Delta G$ relative to (*E*,*E*)-**1** is ~7 kcal/mol based on a 2.3 kcal/mol increment per alkyl group and corresponds to an equilibrium ratio i of ~1.5×10^{-4}.

That (*Z*)-**2** may owe its $\Delta\Delta G$ increment of 1.45 kcal/mol over (*E*)-**2** to nonplanarity is supported by the difference in their ultraviolet absorption spectra ((*Z*)-**2**, λ_{max} 217 nm (ϵ 4400); (*E*)-**2**, λ_{max} 232 nm (ϵ 16 100)), the slower rate of reaction with sulfur dioxide reported for (*Z*)-**2**,[10] and, perhaps, by a difference in boiling point ((*Z*)-**2**, 108 °C; (*E*)-**2**: 127 °C] comparable with that existing between (*E*,*Z*)-**1** and (*E*,*E*)-**1** (Table I). Determination of structure by electron diffraction is desirable.

In the kinetic studies, a stock solution of potassium *tert*-butoxide in HMPA (0.1 M) is used. Consistent with being less rigorously barred from a planar conformation, (*E*,*E*)-**1** reacts more rapidly than (*Z*,*Z*)-**1**. Based on the approximate, reversible model above and starting from (*Z*,*Z*)-**1** or (*E*,*E*)-**1**, the data of Table VI afford a value of $(k_1 + k_{-1}) = 2.85 \times 10^{-5}$ s^{-1}. With the fraction of (*Z*,*Z*)-**1** at equilibrium being 0.123, $k_{-1} = 2.45 \times 10^{-5}$ s^{-1} and $k_1 = 0.40 \times 10^{-5}$ s^{-1}. The slowness of (*Z*,*Z*)-**1** relative to other isomers in base-catalyzed isomerization is likely ascribed to its large deviation from planarity and consequent limitation of stabilization in the intermediate carbanion to an allylic rather than a pentadienylic system.

Enthalpies of Formation of (*E*,*E*)-1, (*E*,*Z*)-1, and (*Z*,*Z*)-1. To remove uncertainties arising from differences in entropies, positions of equilibrium might have been measured at different temperatures, preferably in the gas phase, but we have opted instead to determine enthalpy differences directly from heats of hydrogenation in isooctane at 25 °C. The calorimeter, experimental method, and accuracy of measurements have already been reported.[17] Experimental data are given in Table VII.

Heats of hydrogenation have not been corrected experimentally for differences in enthalpies of solution of the dienes and alkanes because such differences are small in isooctane. That they are approximately proportional to the number of conjugated double bonds and can be adequately approximated by a "double-bond increment" of +0.1 kcal/mol per double bond can be justified by the data collected in Table VIII.

Differences in enthalpies of vaporization between those of the olefins and those of the corresponding alkanes are generally small. Because a linear relation prevails between boiling point and heat of vaporization among structurally related compounds,[18] the required differences in heats of vaporization can be approximated from their boiling points. For the 20 pairs of olefins and their related alkanes collected in Table IX,[19] two-thirds of the calculated corrections fall between −0.22 and +0.51 kcal/mol. From the

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Table VII. Heats of Hydrogenation of **1** and **6**

substr	titr., mol/s × 10^7	catalyst,[a] g	H_2 uptake, mol/s × 10^6	energy, mcal/s	$-\Delta H_H°$, kcal/mol
(*E*,*E*)-**1**	1.0040	0.1046	0.2015	5.0134	49.85
(*E*,*E*)-**1**	1.0040	0.1386	0.1999	5.0116	50.03
(*E*,*E*)-**1**	1.0040	0.1426	0.1998	5.0070	50.00
(*E*,*E*)-**1**	1.0040	0.1426	0.1991	5.0006	50.02
					49.98 ± 0.08
(*E*,*Z*)-**1**	1.0200	0.1093	0.2030	5.3274	52.36
(*E*,*Z*)-**1**	1.0200	0.1003	0.2025	5.3091	52.24
(*E*,*Z*)-**1**	1.0200	0.1000	0.2031	5.3109	52.18
(*E*,*Z*)-**1**	1.0200	0.1046	0.2034	5.2981	52.02
					52.20 ± 0.15
(*Z*,*Z*)-**1**	0.9970	0.0528	0.1931	4.9121	50.88[b]
(*Z*,*Z*)-**1**	0.9970	0.0528	0.1901	4.8759	51.30[b]
(*Z*,*Z*)-**1**	0.9970	0.1043	0.1910	4.8951	51.26[b]
(*Z*,*Z*)-**1**	0.9976	0.0549	0.1993	5.0939	51.09
(*Z*,*Z*)-**1**	0.9976	0.1007	0.1983	5.0633	50.91
(*Z*,*Z*)-**1**	0.9976	0.1007	0.1990	5.0672	50.86
					51.05 ± 0.20
6[c]	0.8980	0.0995	0.1793	5.1899	57.88
6[c]	0.9040	0.5987	0.1807	5.2384	57.58
6[c]	0.9600	0.5958	0.1925	5.5065	57.20
6[c]	0.9690	0.6046	0.1931	5.6303	58.29
					57.74 ± 0.46

[a] Catalyst is Pd/C (10%). [b] Based on consumption of hydrogen. [c] Prepared according to Backer and purified by GC (99.7%): Backer, H. J. *Recl. Trav. Chim. Pays-Bas* **1939**, *58*, 643–661.

Table VIII. Heats of Solution ($\Delta H_{L,\infty\text{-}}{}^{i}$) of Some Olefins and Their Related Alkanes in Isooctane (kcal/mol)[a]

olefin	ΔH_H	alkane	ΔH_L	$\Delta\Delta H_L$	
				exptl[b]	calcd[c]
hept-1-ene	0.06	*n*-heptane	0.01	0.05	0.1
cyclohexene	0.18	cyclohexane	0.15	0.03	0.1
cyclohexa-1,4-diene	0.29			0.14	0.2
cyclohexa-1,3-diene	0.38			0.23	0.2
hexa-1,5-diene	0.22	*n*-hexane	0.00	0.22	0.2
trans-hexa-1,3,5-triene	0.58			0.58	0.3
cycloheptatriene	0.38	cycloheptane	0.13	0.25	0.3
cyclooctatetraene	0.60	cyclooctane	0.15	0.45	0.4
bicyclo[4.4.1]undeca-1,3,5,8-tetraene	0.38	1,6-methanocyclodecane	0.07	0.31	0.4
bicyclo[4.4.1]undeca-1,3,5,7,9-tetraene	0.72			0.65	0.5
1-methylnaphthalene	0.68	*trans*-decalin	0.07	0.61	0.5

[a] Determined by a previously described method.[17] [b] ΔH_L(olefin) − ΔH_L(alkane). [c] Calculated with a "double-bond increment" of 0.10 kcal/mol.

equation for ΔH_V(olefin) − ΔH_V(alkane) derivable from the data in Table IX, corrections, $\Delta\Delta H_V°$, of +0.82, −0.12, and −0.63 kcal/mol for (*E*,*E*)-**1**, (*E*,*Z*)-**1**, and (*Z*,*Z*)-**1**, respectively, are made.

Correction can also be made on the basis of Kovats indices,[20] which, in a series of structurally related substances, are linearly related to boiling points[21] and therefore to heats of vaporization. The validity of this procedure is also demonstrated by data in Table IX. The correction for **6** is made by application of the linear equation deduced in Table IX. The resulting value −0.71 kcal/mol agrees well with the value −0.64 kcal/mol, calculated from boiling points. A correction based on structural increments[22] differs significantly (+0.70 kcal/mol), is considered unreliable, and would have been useless for the isomers of **1** in any event.

The product of hydrogenation of each of the dienes **1** is a mixture of racemic (60%) and meso (40%) 3,4-dimethylhexanes, each of which has been synthesized independently. Calculation by the MM2, molecular mechanics program of Allinger[23] gives values for the heats of formation of the racemic (−51.66 kcal/mol) and meso (−50.37 kcal/mol) isomers. The derived value for the 60:40 mixture, −51.14 kcal/mol, agrees well with an experimental value of −50.88 kcal/mol reported[19] for a mixture of unspecified composition.

Thermochemical data pertaining to (*E*,*E*)-**1**, (*E*,*Z*)-**1**, (*Z*,*Z*)-**1**, and **6** are collected in Table IV. In order to compare the free energy differences with the enthalpic data from the hydrogenation, the value of $\Delta\Delta G$ of (*E*,*Z*)-**1** must be increased by $RT \ln 2$, because both (*E*,*E*)-**1** and (*Z*,*Z*)-**1** have symmetry numbers of 2. Although (*E*,*Z*)-**1** and (*Z*,*Z*)-**1** are safely assumed to be nonplanar and therefore instantaneously chiral, there is little reason to believe that the enthalpies of activation for their racemization would be high enough at 90 °C to require an entropic correction for chirality. Had it been necessary, it would have amounted to 0.50 kcal/mol.

A simple model for the enthalpies of formation[19] (kilocalories per mole) of 1,3-dienes is constructed by removing dihydrogen appropriately from two monoenes. With butadiene as illustration,

$$CH_2{=}CH_2\ (+12.55) + CH_2{=}CH_2\ (+12.55) \rightarrow CH_2{=}CHCH{=}CH_2\ (+26.29) + H_2$$

$\Delta H_r° = +1.19$ kcal/mol. When this imagined reaction is extended to *trans*-piperylene (+18.20), isoprene (+18.04), and 2,3-dimethylbutadiene (+10.78), values of $\Delta H_r°$ of +0.87, +0.71, and +1.22 kcal/mol, respectively, are obtained. A mean value for $\Delta H_r°$ is +1.00 ± 0.25 kcal/mol. This model is intended to represent strain-free dienes containing all available stabilization energy with no limitation on choice of conformation.

Application of this model to the three combinations of *cis*-butene (−2.72) and *trans*-butene (−1.70) generates model enthalpies of formation for (*E*,*E*)-**1**, (*E*,*Z*)-**1**, and (*Z*,*Z*)-**1** of *−2.40*, *−3.42*, and *−4.44* kcal/mol, respectively. Comparison with the experimental values of −0.54, +0.74, and −0.92 kcal/mol, respectively, reveals discrepancies of +1.86, +4.16, and +3.52 kcal/mol, respectively.

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Table IX. Estimation of Differences in Heats of Vaporization (Olefin − Alkane) (kcal/mol) from Boiling Points and Retention Indices

olefin	$\Delta\Delta H_V$ exptl[a]	$\Delta\Delta H_V$ calcd[b]	$\Delta\Delta H_V$ calcd[c]	Δbp	ΔI,[d] exptl
cyclopentene	−0.14	−0.16	−0.11	−5.02	−16
2-methyl-1,3-butadiene	0.37	0.36	0.35	6.22	23
2-methylbut-1-ene	0.15	0.23	0.24	3.31	14
3-methylbut-1-ene	−0.33	−0.28	−0.22	−7.79	−25
2-methylbut-2-ene	0.44	0.57	0.56	10.72	41
benzene	0.19	0.07	−0.03	−0.06	−9
cyclohexa-1,3-diene	0.00	0.06	−0.08	−0.43	−13
cyclohexene	0.10	0.18	0.26	2.23	15
2,3-dimethylbut-2-ene	0.84	0.78	0.78	15.22	59
3,3-dimethylbut-1-ene	−0.24	−0.32	−0.28	−8.50	−30
2,3-dimethylbuta-1,3-diene	0.49	0.57	0.58	10.79	42
hex-1-ene	−0.20	−0.17	−0.14	−5.25	−18
cis-hex-2-ene	0.00	0.08	0.11	0.10	3
trans-hex-2-ene	0.02	0.04	0.05	−0.87	−2
hexa-1,5-diene	−0.38	−0.35	−0.33	−9.28	−34
cis-hex-3-ene	−0.05	−0.03	−0.06	−2.30	−7
trans-hex-3-ene	0.02	0.00	−0.06	−1.66	−7
1-methylcyclohexene	0.61	0.49	0.48	9.07	34
toluene	0.63	0.52	0.47	9.70	33
cycloheptatriene	0.04	−0.09	−0.14	−3.50	−18
(*E*,*E*)-**1**		0.82		16.8	
(*E*,*Z*)-**1**		−0.12		−4.2	
(*Z*,*Z*)-**1**		−0.63		−15.2	
6		−0.64	−0.71[e]	−15.6	−66[f]

[a] Reference 19. [b] Calculated following Wadsö[18] from Δbp with $y = a + bx$, where $a = 0.0756$, $b = 0.0461$, and $r = 0.973$. [c] Calculated according to Wehrli and Kováts[20] from ΔI (retention indices) with $y = a + bx$, where $a = 0.0745$, $b = 0.0119$, and $r = 0.946$. [d] Hively, R. A.; Hinton, R. E. *J. Gas Chromatogr.* **1968**, *6*, 203–267. [e] Bp(cor): **6**, 179.1 °C; 2,3-di-*tert*-butylbutane, 194.7 °C. [f] I^{120}(0V101): **6**, 1022.5; 2,3-di-*tert*-butylbutane, 1088.6.

The larger discrepancies exhibited in the nonplanar dienes (*E*,*Z*)-**1** and (*Z*,*Z*)-**1** are comparable in magnitude with the (negative) energy of conjugation originally identified in butadiene by Kistiakowsky[4] and associated with π-electron delocalization. The appearance of these (positive) discrepancies is consistent with enthalpy of conjugation requiring planarity as first enunciated by Hückel.[5] In respect of the Dewar–Schmeising hypothesis,[3] it is reasonable to conclude that the major source of energy of conjugation is not the angular-independent, sp^2–sp^2 σ interaction, which would have remained operative in (*E*,*Z*)-**1** and (*Z*,*Z*)-**1**.

The discrepancy revealed by (*E*,*E*)-**1** should, in this analysis, have been zero. Its positive, if smaller, value is ascribed conjecturally to enthalpy-raising, secondary, steric interactions arising from a partially thwarted struggle to achieve coplanarity and maximum π-electron delocalization. The deviation from coplanarity (26.6°) in (*E*,*E*)-**1** likely reflects a compromise between an energy-raising steric factor, which appears to vanish at larger dihedral angles ((*E*,*Z*)-**1**, (*Z*,*Z*)-**1**), and enthalpy-lowering resonance stabilization, which is maximized in the antiperiplanar conformation.

That qualitative arguments are incapable of furnishing a quantitative understanding of the discrepancy (+1.86 kcal/mol) is sharply emphasized when one tries to rationalize the large, positive discrepancy shown by **6** (+10.95 kcal/mol: 3,3-dimethylbut-1-ene (−14.46 kcal/mol),[19] imagined **6** (*−27.92* kcal/mol), experimental **6** (−16.97 kcal/mol)).

For the moment, the new experimental enthalpies of formation of these nonplanar dienes of known dihedral angle augment those already in the literature (e.g., cyclohexa-1,3-diene,[19,24a] cycloocta-1,3-diene,[25,24b] cyclooctatetraene[19,24c]) and will, we hope, contribute ultimately to development of a reliable molecular mechanical recipe, cum or sine quantum mechanical component, for calculation of enthalpies of formation of both planar and nonplanar conjugated dienes and polyenes.

Experimental Section

Infrared spectra are recorded on a Perkin-Elmer 598 spectrophotometer, samples as thin films on NaCl plates. ^{1}H NMR spectra in CDCl$_3$ solution are recorded on Varian FT-80 or JEOL FX-270 spectrophotometers and are reported (ppm) relative to internal TMS; ^{13}C NMR spectra are recorded on the JOEL FX-270 at 67.8 MHz and are calibrated against the solvent signal.

Spinning band distillations are performed on a glass B/R 8 Microstill with a 9-in. Teflon band operating at 3000 rpm and ~12 theoretical plates.

Preparative-scale GC separations are effected on a Varian Aerograph A90-P3 chromatograph with thermal conductivity detector: column A, $^3/_8$ in. × 5 m, 10% β,β′-oxydipropionitrile on 60–80 mesh Kieselguhr; column B, $^1/_4$ in. × 2 m, 25% Carbowax 20M on 60–80 mesh Chromosorb A; column C, $^1/_4$ in. × 3 m, 10% JXR on 60–80 mesh Chromosorb-P.

Analytical GC employs a Perkin-Elmer 990 instrument with flame-ionization detector and a Hewlett-Packard 3380S integrator: column D, 300 ft × 0.01 in. Perkin-Elmer Carbowax (K-20) capillary; column E, 70 m × 0.01 in., OV 101 glass capillary.

3,4-Dimethylhexa-2,4-dienes (1) by Dehydration of 3,4-Dihydroxy-3,4-dimethylhexane. (a) Pyrolysis over Alumina at 500 °C. The mixed diols (90 g, 0.62 mol)[26,27] are distilled at 0.1 mm into a tube heated at 500 °C and packed with activated alumina (8–15 mesh). The effluent gases are condensed in traps cooled by dry ice (guard against plugging by ice). Distillation through a 1-ft Vigreux column affords a mixture of olefins (55.8 g, 0.51 mol, 82% of theoretical).

(*Z*,*Z*)-3,4-Dimethylhexa-2,4-diene ((*Z*,*Z*)-**1**) is concentrated in fractions boiling at 107–109 °C by distillation in the spinning band column. Enriched (*Z*,*Z*)-**1** (6.4 g) is heated with maleic anhydride (5.5 g) at 110 °C for 5 h in a sealed tube. Vacuum transfer of unreacted olefin affords 2.0 g of (*Z*,*Z*)-**1** of >95% purity. Fractions of bp 109–121 °C consist mainly of (*E*,*Z*)-**1** (~11 g), while those of bp 134–135 °C consist mainly of (*E*,*E*)-**1** (>95%, ~11 g). Final purification of the olefins may be effected by GLC on column A.

(b) Heating with Iodine. In a procedure modified from that of Reeve and Reichel,[10] 100 g (0.684 mol) of diol, heated with 0.50 g of I$_2$, affords 39 g (52%) of colorless product, bp 108–136 °C, on distillation.

(*Z*,*Z*)-3,4-Dimethylhexa-2,4-diene ((*Z*,*Z*)-1) from (*Z*)-2-Bromo-2-butene. Pursuant to the procedure of Denney and Davis,[8] (*Z*)-2-bromo-2-butene (24.3 g, 0.18 mol) is converted to an ethereal solution 0.61 M in (*E*)-2-lithio-2-butene (68%) and treated with anhydrous cobaltous chloride[8] (11.68 g, 0.09 mol). Careful removal of solvent (1-ft Vigreux column; head temperature <35 °C) and short-path distillation of the residue give a fraction: bp 100–110 °C, 2.40 g (42%). Analysis by capillary GC (column C: 75 °C, 25 psi He) reveals (*Z*,*Z*)-**1** (82.5%), (*E*,*Z*)-**1** (11.2%), and (*E*,*E*)-**1** (3.5%). Concentrated to >95% purity by spinning band distillation (bp 102.0–102.3 °C (lit.[10] bp 104 °C)), (*Z*,*Z*)-**1** (>99%) is obtained by GC separation on column B (70 °C, 60 mL of He/min).

(*Z*)-3,4-Dimethylhexa-1,3-diene ((*Z*)-3). A 1.00-mL sample of (*E*,*Z*)-**1** (97.1% purity) is degassed by several freeze–thaw cycles and sealed in vacuo in a 10-mL, thick-walled Pyrex tube, previously soaked in 10% aqueous NaOH, rinsed with distilled water, and oven-dried. After having been heated at 209 ± 3 °C in a tube furnace for 12 h, the tube is opened. The 980 μL of recovered, colorless liquid is revealed on analysis by capillary GC (column C: 40 °C, 20 psi He) to consist of 81.1% (*E*,*Z*)-**1**, 5.9% (*Z*,*Z*)-**1**, and 11.8% (*Z*)-**3**. Purification by preparative GC on column A (95 °C, 46 mL of He/min) affords (*Z*,*Z*)-**1** (25 μL; t_R, 10.2 min), (*E*,*Z*)-**1** (520 μL; t_R, 12.0 min), and (*Z*)-**3** (70 μL; t_R, 27 min).

(*Z*)-**3** has the following spectra: ^{1}H NMR (CDCl$_3$, 270 MHz) 6.85 (dd, 1 H, J = 10.88, 17.14 Hz), 5.11 (d, 1 H, J = 17.14 Hz), 4.96 (d, 1 H, J = 10.88 Hz), 2.20 (q, 2 H, J = 7.58 Hz), 1.79 (s, 3 H), 0.99 (d, 3 H, J = 7.58 Hz); ^{13}C NMR (CDCl$_3$) 137.4 (s), 135.4 (d), 120.5 (s), 110.8 (t), 27.1 (t), 19.4 (q), 13.6 (q), 13.2 (q); UV, λ_{max} 241 nm (ε 20 300) (CH$_3$CN).

(*E*)-3,4-Dimethylhexa-1,3-diene ((*E*)-3). An 80-μL sample of (*Z*)-**2** (91.6% purity) is sealed in vacuo in a 2-mL Pyrex tube (prepared as in the preceeding experiment) and heated in a tube furnace at 208 ± 1 °C for 31.3 h. After the tube has been cooled to room temperature, its tip is scored, frozen in liquid N$_2$, and detached. The product (70 μL) is shown by capillary GC (column A: 40 °C, 20 psi He) to consist of 48.2%

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(*Z*)-**2** and 39.8% (*E*)-**3**. Purification is effected by preparative GC on column A (100 °C, 50 mL/min He): (*Z*)-**2**: 30 μL; t_R, 12.4 min; (*E*)-**3**: 20 μL; t_R, 34.9 min.

(*E*)-**3** has the following spectra: ^{1}H NMR (CDCl$_3$, 270 MHz) 6.84 (dd, 1 H, J = 10.87, 17.14 Hz), 5.11 (d, 1 H, J = 17.14 Hz), 4.98 (d, 1 H, J = 10.87 Hz), 2.15 (q, 2 H, J = 7.58 Hz), 1.82 (s, 3 H), 1.77 (s, 3 H), 0.99 (t, 3 H, J = 7.58 Hz); ^{13}C NMR (CDCl$_3$) 139.1 (s), 136.1 (d), 120.5 (s), 111.0 (t), 28.6 (t), 17.9 (q), 12.9 (q), 12.4 (q); UV, λ_{max} 241 nm (ϵ 18 900) (CH$_3$CN).

Properties of 3,4-Dimethylhexa-2,4-dienes. Refractive indices are measured on a Bausch and Lomb type 33-45-58 Abbé refractometer corrected to the sodium D line at 20.0 ± 0.2 °C. Calibration ($n^{20}{}_D$) employs 1-bromonaphthalene (1.6584), carbon tetrachloride (1.4602), and acetone (1.3591) (lit.[28] 1.658, 1.4603, and 1.3591, respectively). Densities are measured at 20.4 ± 0.3 °C in a Misco 10-μL micropycnometer, calibrated by water to have an exact volume of 9.865 μL and checked against toluene, $d^{20.4}$ = 0.8662 (lit.[28] d^{20} 0.8669). Molar refraction is calculated by the Lorentz–Lorenz equation. Results are given in Table I.

Thermal Rearrangements of (*E*,*Z*)- and (*Z*,*Z*)-3,4-Dimethylhexa-2,4-diene and (*Z*)-3,4-Dimethylhexa-1,3-diene (*E*,*Z*)-1, (*Z*,*Z*)-1, (*Z*)-3).[29] Heating is carried out in medium-walled Pyrex tubes (soaked several days in aqueous 15% NaOH, rinsed repeatedly with distilled water, and oven-dried), 0.6 cm (i.d.) × 8 cm of approximately 2-mL volume. The tubes are heated in the vapors of boiling tetrahydronaphthalene (207.5–208 °C), temperature being monitored by an iron-constantan thermocouple. Samples of diene in 15-μL portions are degassed by several freeze–thaw cycles prior to being sealed under vacuum. The sealed tubes are suspended in the hot vapor bath for the desired length of time, removed, plunged into ice–water, frozen in liquid nitrogen, opened, and then sealed with a septum. By means of a syringe, 200 μL of pentane and 5 μL of a standard mixture of *cis*- and *trans*-decalin are added in the case of (*E*,*Z*)-**1**, and the resulting mixtures are analyzed by capillary GC (column D). In the cases of (*Z*,*Z*)-**1** and (*Z*)-**3**, 100 μL of ether and 5 μL of *n*-nonane as internal standard are added, and the mixtures are analyzed by capillary GC (column E).

Results combined from several runs are given in Table V. Rate constants are calculated by a SIMPLEX program, which minimizes the residues between experimental and calculated concentrations. The specific rate constants and positions of equilibria are given in Figure 2.

Thermal Isomerization of (*Z*)-3-Methyl-4-methylenehex-2-ene ((*Z*)-2). Samples of (*Z*)-**2** (97.7% purity) are prepared in the manner above and heated at 208.3 ± 0.4 °C for 24, 48, 72, and 164 h, respectively. The contents of the tube are analyzed by column E and are found to consist of (*Z*)-**2** (55.86 ± 0.25%) and (*E*)-**3** (44.14%), between which equilibrium is already established after 24 h; $K_{208\,^\circ C}((Z)\text{-}\mathbf{2}/(E)\text{-}\mathbf{3})$ = 1.266 ± 0.012.

Base-Catalyzed Equilibrations of 3,4-Dimethylhexa-2,4-dienes. Solutions of sublimed potassium *tert*-butoxide (0.65 g) in HMPA (50 mL), freshly distilled from molecular sieves at 25 mm, are prepared in a drybox. "Preampules" consist of 8-mm tubing rounded at one end, closed with a rubber septum at the other end, and made with a constriction that produces an ampule 8-10 cm in length after being sealed. For equilibrations, 250 μL of HMPA is injected into the bottom of the preampule followed by 30 μL of diene, 5 μL of *n*-octane as internal standard, and 250 μL of potassium *tert*-butoxide 0.1 M in HMPA. The lower portion of the preampule is cooled in dry ice, evacuated, and sealed. The ampules are then heated at 90 ± 0.1 °C for varying periods of time. The samples of (*E*,*E*)-**1** and (*E*,*Z*)-**1** become orange-brown after 3 days' heating, whereas solutions of (*Z*,*Z*)-**1** remain colorless.

For analysis, the contents of the ampules are diluted with water, extracted with pentane, and analyzed by GC on column A. Relative sensitivities are determined in order to provide correction factors to the analytical data: $s = [(\mathrm{wt}_x)(\mathrm{area}_{std})/(\mathrm{wt}_{std})(\mathrm{area}_x)]$. Relative to *n*-octane, values of s for (*E*,*E*)-**1**, (*E*,*Z*)-**1**, (*Z*,*Z*)-**1**, and (*E*)-**2** are 1.055, 1.09, 1.12, and 1.11, respectively.

In order to determine equilibrium concentrations, a temperature of 90 °C and times of reaction ranging from 30–170 h are needed owing to the slowness with which (*Z*,*Z*)-**1** reacts. At least four independent runs are made with each of four dienes. The resulting fractions at equilibrium relative to (*E*,*E*)-**1** and relative retention times on column B are given in Table III.

Two kinetic runs have been made under the same conditions as the equilibrations, one starting with pure (*E*,*E*)-**1**, the other with pure (*Z*,*Z*)-**1**. All tubes are placed in the bath at 90 °C at the same time. As tubes are removed, cooled, opened and their contents transferred to a small separatory funnel with pentane and water, a weighed amount of *n*-octane is added. Results of three analyses of each solution by GC on column B are given in Table VI.

The data relating change in concentration of (*Z*,*Z*)-**1** with time can be handled as a simple reversible system with the equation $\ln [(T_e - T_0)/(T_e - T_i)] = a_0 + (k_1 + k_{-1})t_1$, where T_e, the fraction of (*Z*,*Z*)-**1** at equilibrium, is taken from the experiment of longest duration to be 0.123, T_0 is the fraction of (*Z*,*Z*)-**1** at the start, and T_i is the fraction at time t_i. With (*E*,*E*)-**1** as starting material, $k_1 + k_{-1} = (2.85 \pm 0.15) \times 10^{-5}$ s^{-1} (r^2 = 0.992); with (*Z*,*Z*)-**1** as starting material, $k_1 + k_{-1} = (2.85 \pm 0.25) \times 10^{-5}$ s^{-1} (r^2 = 0.985). This close agreement further justifies the assumption that equilibrium has been established among all the other components.

Catalytic Hydrogenation of the 3,4-Dimethylhexa-2,4-dienes. Prior to catalytic hydrogenation, samples are carefully repurified by GC on column C at 80 °C and analyzed on column E at 60 °C: (*E*,*E*)-**1**, 99.4% purity; (*E*,*Z*)-**1**, 99.9%; (*Z*,*Z*)-**1**, 99.7%. In all instances, uptake of hydrogen is quantitative. Experimental data are given in Table VII.

Corrections for differences in heats of solution of the olefin and alkane are based on the data and procedure in Table VIII.

Corrections for differences in heats of vaporization are based on the data and procedures contained in Table IX.

Preparation of *rac*- and *meso*-3,4-Dimethylhexanes. Into a solution of 10 g of *trans*-4,5-dimethylcyclohexene[30] in 150 mL of THF at −70 °C is passed slowly (30 L/h) a stream of ozone until an attached KI solution turns dark brown (ca. 1 h). After removal of excess ozone with a stream of nitrogen, the solution at −40 °C is added dropwise to a suspension of 25 g of lithium aluminum hydride in 300 mL of THF. After being stirred for 3 h at −20 °C, the solution is hydrolyzed with saturated aqueous Na$_2$SO$_4$ at 0 °C. After the usual workup, the crude product (10 g) is dissolved in 100 mL of pyridine and the resultant solution is added dropwise at −10 °C to a solution of 30 g of *p*-toluenesulfonyl chloride in 60 mL of pyridine. After 4 h, the reaction mixture is poured onto ice and worked in the usual manner. Without further purification, the crude product (25 g) is dissolved in 150 mL of THF and the resultant mixture added to a solution of 15 g of lithium aluminum hydride in 300 mL of THF. After 6 h of boiling under reflux, water (0 °C) is added, and the mixture is extracted with three 100-mL portions of pentane. After concentration and separation by GC, *rac*-3,4-dimethylhexane is obtained: t_R, 152 min on capillary column (OV 101, 150 m, glass, 25 °C); IR, 2986, 2940, 2880, 1460, 1380 cm^{-1}; ^{1}H NMR 0.7–1.0 (m, 12 H), 1.1–1.5 (m, 6 H); ^{13}C NMR, 38.35, 27.52, 14.61, 12.12; MS, *m/e* 114 (M$^+$).

Starting with *cis*-4,5-dimethylcyclohexene[30] and following the same procedure furnishes *meso*-3,4-dimethylhexane: t_R, 151 min; IR, 2983, 2938, 2880, 1465, 1432 cm^{-1}; ^{1}H NMR, 0.7–1.0 (m, 12 H), 1.1–1.6 (m, 6 H); ^{13}C NMR, 39.29, 25.62, 16.04, 12.12; MS, *m/e* 114 (M$^+$).

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Registry No. (*E*,*E*)-**1**, 18265-39-9; (*E*,*Z*)-**1**, 2417-88-1; (*Z*,*Z*)-**1**, 21293-01-6; (*E*)-**2**, 32388-98-0; (*Z*)-**2**, 32388-99-1; (*Z*)-**3**, 112655-32-0; (*E*)-**3**, 112655-33-1; **4**, 16356-05-1; **5**, 90154-44-2; (±)-(*R**,*R**)-3,4-dimethylhexane, 52919-17-2; (*R**,*S**)-3,4-dimethylhexane, 52949-33-4; (±)-(*R**,*R**)-3,4-di-*tert*-butylbutane, 112655-34-2; 3,4-dihydroxy-3,4-dimethylhexane, 1185-02-0; (*Z*)-2-bromo-2-butene, 3017-68-3; (*E*)-2-lithio-2-butene, 28944-86-7; *trans*-4,5-dimethylcyclohexene, 3685-01-6; *cis*-4,5-dimethylcyclohexene, 3685-00-5.

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