injected.<sup>20</sup> The cell was shaken with a standard laboratory shaker. After the shaker was switched off, data from the conductivity amplifier were recorded on millimeter graph paper with a Phillips PM8041 recorder (maximum chart speed 2 cm s<sup>-1</sup>).

Experimental conditions for each solvent composition and temperature were optimized within the following general constraints. The cell was shaken briefly, and the shaker was then switched off before satisfactory conductance readings were made. The shaking process causes at least a ripple and often more extensive oscillation of the conductance reading. The vigor of and length of time for shaking were varied and must be sufficient to dissolve the compound rapidly, so that acceptable kinetic runs showed no "drift" of the infinity conductances.<sup>2f</sup> For the faster kinetic runs the recorder and the shaker were first switched on; the acetone solution was then injected, while simultaneously the shaker was switched off. The zero time for the kinetic run was taken after the conductance readings became steady, and  $15\mathchar`-25$ data points about equally spaced in conductance were read from the chart on at least one of the millimeter grid lines and with the aid of an 8× magnification chart reader. Satisfactory rate constants could be obtained if there was at least a 1-2-cm change in the conductance scale after the zero time. In the fastest reaction for which satisfactory results were obtained (1-adamantyl mesylate

in 20% acetone/water at 14.9 °C;  $t_{1/2}\approx0.4$  s), the zero time was 0.6 s after the start of the injection, and the first 50% of the total reaction was excluded from the calculations of kinetics. During the optimization process for each of the faster kinetic runs, a significant number of runs had to be discarded, usually by inspection of the recorder trace (e.g., drift of infinity conductance) but occasionally after attempts to refine the data by computer. Many attempts to follow even faster reactions  $(t_{1/2}\approx 0.2~{\rm s})$  in continuously stirred solutions (as in method A, discussed previously<sup>8</sup>) were unsuccessful; although the data appeared to be satisfactory, the rate constants were 30-100% lower than the values obtained by temperature extrapolation; such erroneous results, presumably caused by substrates dissolving during the kinetic run, have been discussed previously.<sup>2f</sup>

Slower kinetic runs ( $t_{1/2} \approx 120$  s) were monitored by using a Wayne Kerr Model B331 autobalance conductance bridge, but the conductivity amplifier/chart recorder procedure is satisfactory for long kinetic runs  $(t_{1/2} \approx \text{several hours}).^8$ 

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Registry No. I-OMs, 25236-60-6; I-OTs, 16200-57-0; II-OMs, 31616-68-9; II-OTs, 25139-43-9; methanol, 67-56-1; ethanol, 64-17-5; water, 7732-18-5; 2-propanol, 67-63-0; tert-butyl alcohol, 75-65-0; 2,2,2-trifluoroethanol, 75-89-8; 1,1,1,3,3,3-hexafluoroisopropyl alcohol, 920-66-1; acetic acid, 64-19-7; formic acid, 64-18-6; trifluoroacetic acid, 76-05-1.

# Equilibration of 5-Methyl-3-hexen-2-one and 5-Methyl-4-hexen-2-one and of XCH<sub>2</sub>CH=CYZ/XCH=CHCHYZ Pairs in General<sup>1</sup>

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The equilibrium constant for isomerization of 5-methyl-4-hexen-2-one to trans-5-methyl-3-hexen-2-one in tert-butyl alcohol at 25 °C has been found to be 0.40, which is smaller by 250-fold than a literature value. This and other equilibrium constants for reactions of the type  $XCH_2CH = CMe_2 \Rightarrow XCH = CHCHMe_2$  are shown to be consistent with the double bond stabilizing abilities of various groups as measured by equilibrium constants for reactions of the type  $XCH_2CH=CHY = XCH=CHCH_2Y$ . The general case of isomerizations of the type  $XCH_2CH=CYZ = XCH=CHCHYZ$  is also discussed.

Equilibrium constants for reactions of the type shown in eq 1 can be correlated in terms of  $D_X$  and  $D_Y$ , the double

$$trans-XCH_2CH=CHY \rightleftharpoons trans-XCH=CHCH_2Y$$
 (1)

bond stabilizing parameters for X and Y.<sup>2</sup> It is expected that  $D_X$  will be useful in correlating data on other processes in which the XCH<sub>2</sub>CH=C group is transformed to a trans-XCH=CHCH group. Siroký and Procházka have combined their data with literature data to report that equilibrium constants for reactions of the type shown in eq 2 are fairly linearly correlated with those for reactions

$$XCH_2CH = CMe_2 \rightleftharpoons XCH = CHCHMe_2$$
 (2)

of the type shown in eq 3, except for the case where X is

$$XCH_2CH = CHMe = XCH = CHCH_2Me$$
 (3)

hydrogen.<sup>3</sup> For the reaction where X is acetyl, they noted a failure to achieve equilibration.<sup>4</sup> There is a recently reported equilibrium constant of 100 for this reaction, the isomerization of 5-methyl-4-hexen-2-one (1) to 5-methyl-3-hexen-2-one (2).<sup>5</sup> This value, when combined with

$$\frac{\text{Me}_2\text{C}=\text{CHCH}_2\text{Ac}}{1} \stackrel{\text{c}}{=} \frac{\text{Me}_2\text{CHCH}=\text{CHAc}}{2}$$
(4)

subsequent data on the isomerization of 4-hexen-2-one to 3-hexen-2-one, gives a major deviation from their correlation. We thought it unlikely that equilibrium 2 would lie much further to the right when X is acetyl than when

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<sup>(20)</sup> A typical injection was 2–5  $\mu$ L, but in some difficult cases 20  $\mu$ L of a very dilute acetone solution was injected. The corresponding change in solvent composition leads to <5% error in the rate constant. In general, 1-adamantyl mesylate dissolved more readily in acetone > ethanol > trifluoroethanol.

<sup>(1)</sup> (a) This research was supported in part by National Science Foundation Grant CHE 79 26319. Part 27 in the series "Structural Effects on Rates and Equilibria". (b) For part 26 see: Hine, J.; Skoglund, M. J. J. Org. Chem. 1982, 47, 4766-70. (2) Hine, J.; Flachskam, N. W. J. Am. Chem. Soc. 1973, 95, 1179-85.

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Table I.	Equilibrium	Constants for	Reactions of the	Type XCH	CH=CMe	$\Rightarrow$ XCH=CHCHMe <sub>2</sub>
				* *		4

X	% product trans	medium	temp, °C	K	∆G <sup>chem</sup> , kcal/mol	ref
Н	a	b	20	0.01	3.32 <sup>c,d</sup>	3, 9
	a	gas	<b>25</b>	$0.0028^{e}$	$4.14^{d,e}$	16
$\mathbf{Me}$	86	Me <sub>2</sub> SO	55	0.090	1.57	10
	86	Me <sub>2</sub> SO	30	0.079	1.53	5
Ph	99.2	Me <sub>2</sub> SO	30	1.82	-0.36	5
	f	MeOH	20	$1.53^{g}$	$-0.25^{g}$	3, 11
Ac	h	t-BuOH	25	0.40	0.54	i
	99.5	Me <sub>2</sub> SO	30	100	-2.77	5
$NO_2$	h	THF	20	0.52	0.38	3, 15
CO,-	f	H,O	100	0.14	1.46	3
-	f	H,O	20	0.03 <sup>j</sup>	$2.32^{j}$	3, 13
	f	нjo	20	$0.18^{j}$	$1.00^{j}$	3, 14
BuS	91 <sup>k</sup>	Me <sub>2</sub> SO	20	0.063	1.61	3
CO, Et	f	$(Me_2N)_3PO^l$	20	0.20	0.94	3
CN	$75^{m}$	t-BuOH	30	0.32	0.69	12

<sup>a</sup> No cis-trans isomerism is possible. <sup>b</sup> Not stated in the references available to us. <sup>c</sup> Obtained by changing the value of 11.2 kJ/mol in ref 3 to kcal/mol and making the symmetry correction. <sup>d</sup>  $K_{chem} = 3K_{obsd}$ . <sup>e</sup> Calculated from  $\Delta H$  and  $\Delta S$  values obtained from equilibrium constants measured at 268-430 °C. <sup>f</sup> Treated as if 100% trans. <sup>g</sup> Extrapolated by Siroký and Procházka from data at 165 °C.<sup>11</sup> <sup>h</sup> Not determined. <sup>i</sup> Present work. <sup>j</sup> Extrapolated by Siroký and Procházka from data at 100 °C.<sup>13,14</sup> <sup>k</sup> This is the percent present at "equilibrium" for positional isomerization. With iodine as a catalyst, cis-trans isomerization gave 59% trans at equilibrium at room temperature. <sup>l</sup> Using 1 M ester and 1 M t-BuOK. The possibility that significant amounts of the conjugate base of the ester were formed was not mentioned. <sup>m</sup> The average value from the range 65-85%.

it is phenyl or nitro while equilibrium 3 lies further to the right for the phenyl and nitro cases than for the acetyl case. Therefore, we have redetermined the equilibrium constant for isomerization of 1 and 2.

The previous study was carried out in dimethyl sulfoxide solution at 30 °C for 30 min in the presence of excess potassium tert-butoxide, but very little experimental detail was given. The acidities of 1 and 2 should certainly be greater than that of acetone, whose  $pK_a$  in dimethyl sulfoxide is 26.5, and probably nearer that of benzyl methyl ketone  $(pK_a = 19.8)$ ,<sup>7</sup> which is around 10<sup>10</sup> times as acidic as tert-butyl alcohol in dimethyl sulfoxide.8 Therefore, the ketones would be expected to be present largely as their potassium salts under the equilibration conditions. To avoid such complications, we carried out the equilibrations in tert-butyl alcohol using 1,8-diazabicyclo[5.4.0]undec-7ene (DBU) as a catalyst. Equilibrium was approached from both sides. Reaction mixtures were quenched with aqueous acid and extracted with ether. After removal of most of the ether, the residues were analyzed by <sup>1</sup>H NMR measurements on each of the methyl peaks. Experiments using known mixtures showed that this workup procedure did not detectably change the composition of the mixtures. The 2 used was shown to be trans by its 16-Hz CH=CH coupling constant. In none of the spectra could peaks clearly attributable to the cis isomer be seen. The <sup>1</sup>H NMR peaks of 2 used to determine the equilibrium constant were assumed to arise solely from the trans isomer. The equilibrium constant (2/1) was found to be 0.40 at 25 °C and 0.44 at reflux ( $\sim 85$  °C). We estimate the uncertainty from all sources to be about 10%. These data give  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  values of  $0.3 \pm 0.5$  kcal/mol and  $-0.7 \pm 1.4$ eu.

### Discussion

The equilibrium constant we have obtained for reaction 4 is only  $1/_{250}$  of the value reported earlier,<sup>5</sup> and it gives much better agreement with Siroký and Procházka's correlation of equilibrium constants for reaction 2 with

those for reaction 3. In addition, we think that the correlation is probably better for the case where X is hydrogen than is suggested by the data they quote. These data are from a source<sup>9</sup> that is not available to us but that appears to be a secondary source. In Table I is a compilation of equilibrium constants for reactions of the type shown in eq 2, where the reactant is trans. Siroký and Procházka considered the total, cis plus trans, reaction. In the present case it makes little difference but we will continue our preference for minimizing complications arising from cis interactions. We list data from all the sources<sup>3,9-15</sup> quoted by Siroký and Procházka, as well as additional sources. Extrapolation to 25 °C of equilibrium constants determined over the range 268-430 °C for the case where X is hydrogen<sup>16</sup> gives a  $\Delta G^{\text{chem}}$  value of 4.14 kcal/mol, which is near the value (4.26 kcal/mol) that may be calculated from the thermodynamic functions of the two species involved.<sup>17</sup> We have used this value in our subsequent calculations. For the cases where X is methyl and phenyl we have used  $\Delta G^{\text{chem}}$  values (1.53 and 0.36 kcal/mol, respectively)<sup>5</sup> determined at 30 °C because this is nearer our standard reference temperature of 25 °C, but these values differ little from those used earlier. For the acetyl substituent we used our own value. The equilibrium in the case where X is a nitro group had been studied earlier by Procházka and co-workers, who observed complications arising from side reactions.<sup>15</sup> We have used the equilibrium constant extrapolated to 20 °C by Siroký and Procházka,

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Table II. Correlations of  $\triangle G^{\text{chem}}$  Values for Eq 2

x	$\Delta G^{ m chem}$ (eq 2), kcal/mol	C' <sub>Me2</sub> (eq 10)	C' <sub>Me2</sub> (eq 11)	${}_{\Delta}G^{ m chem}$ (eq 3), $^a$ kcal/mol	$\Delta G^{ m chem}( m eq~3) - \ \Delta G^{ m chem}( m eq~2), \  m kcal/mol$
H	4.14	4.53	4.14	2.95	1.19
Me	1.53	4.76	4.44	0.00	1.53
Ph	-0.36	4.41	4.17	-1.83	1.47
Ac	0.54	4.38	4.37	-0.92	1.46
NO <sub>2</sub>	0.38	4.30	4.77	-1.48	1.86
$\operatorname{Bu} \operatorname{S}^{b}$	1.61	4.68	4.63	$-0.18^{b}$	1.79
$CO_2Et$	0.94	4.54	4.30	$-0.94^{c}$	1.88
CN	0.69	3.95	4.16	-1.48	1.86
CO <sub>2</sub> -	1.46	5.77	5.52	-0.77	2.23
$\mathbf{av}^d$ ( $\sigma$ )		4.44(0.25)	4.37 (0.23)		1.53 (0.30)

<sup>a</sup> These values are from ref 18, except as noted. <sup>b</sup> The values of  $D_X$  and of  $\Delta G^{\text{chem}}$  (eq 3) were those for the case where X is MeS. <sup>c</sup> The value where X is CO<sub>2</sub>Me. <sup>d</sup> Not including the case where X is CO<sub>2</sub><sup>-</sup>. When this case is included, the averages (standard deviations) become 4.59 (0.50), 4.50 (0.44), and 1.61 (0.37), respectively.

even though we get substantially different values by treating the data in Tables I and II of the original study<sup>15</sup> ourselves. We also used data obtained by Procházka and co-workers for the cases where X is  $CO_2^{-,3}$  BuS,<sup>3</sup>  $CO_2$ Et,<sup>3</sup> and CN.<sup>12</sup>

Although eq 2 is not a reaction of the type (eq 1) that our previous correlation<sup>2</sup> was devised to fit, the reasoning we used previously plus additional approximations may be used to treat a more broadly defined type of reactions, of which eq 2 is a special case. Let us consider a set of equilibria of the type shown in eq 5, where X is varied but

$$\xrightarrow{H} c = c < \xrightarrow{Y} \longrightarrow \xrightarrow{H} c = c < \xrightarrow{C H Y Z}$$
(5)

Y and Z are held constant. The fact that the XCH<sub>2</sub> group can rotate so as to orient the X group away from the Z group lets us hope that direct interactions between the XCH<sub>2</sub> and Z groups will often be fairly nearly constant if there are no substantial attractive interactions such as hydrogen bonding between X and Z. When Z is hydrogen, as in eq 1, or when Y and Z are both methyl, as in eq 2, this hope seems particularly likely to be realized. A derivation (in the Appendix) in terms of a group contribution correlation gives eq 6, in which  $\Delta G^{\text{chem}}$  is the statistically

$$\Delta G^{\text{chem}} = C_{\text{YZ}} - D_{\text{X}} + I^{\text{t}}_{\text{X,CHYZ}} - I^{\text{t}}_{\text{Y,CH}_{2}\text{X}} - I^{\text{c}}_{\text{Z,CH}_{2}\text{X}}$$
(6)

corrected value of  $\Delta G^{\circ}$  for eq 5,  $C_{YZ}$  is a constant whose value depends only on the nature of Y and Z,  $D_X$  is the double bond stabilizing parameter for X, and the *I* terms are energies of interaction of the subscripted pair of groups across the carbon-carbon double bond (cis or trans, as indicated by the superscript). In the present case, where Y and Z are both methyl groups, eq 6 becomes eq 7. Let

$$\Delta G^{\text{chem}} = C_{\text{Me}_2} - D_{\text{X}} + I^{\text{t}}_{\text{X},\text{Pr-}i} - I^{\text{t}}_{\text{Me},\text{CH}_2\text{X}} - I^{\text{c}}_{\text{Me},\text{CH}_2\text{X}}$$
(7)

us assume that  $I^c_{Me,CH_2X}$  contains a constant component plus a component whose magnitude changes with the nature of X in exactly the same way that  $I^c_{Me,CH_2X}$  does (eq 8). We have previously assumed that  $I^c_{Y,CH_2X}$  may be

$$I^{c}_{Me,CH_{2}X} = I^{co}_{Me,CH_{2}X} + I^{c}_{Me,CH_{2}X}$$
(8)

expressed as shown in eq 9, in which the  $\sigma$ 's are Hammett

$$I^{t}_{Y,CH_{2}X} = \tau_{v}\sigma_{Y}\sigma_{CH_{2}X}$$
(9)

para substituent constants and  $\tau_v$  is a proportionality constant whose least-squares best value is 10.0 kcal/mol.<sup>1b</sup> These assumptions give eq 10, in which  $C'_{\rm Me_2}$  is equal to

$$\Delta G^{\text{chem}} = C'_{\text{Me}_2} - D_{\text{X}} + \tau_{\text{v}} (\sigma_{\text{X}} \sigma_{\text{Pr} \cdot i} - 2\sigma_{\text{Me}} \sigma_{\text{CH}_2 \text{X}}) \quad (10)$$

 $C_{\rm Me_2}$  plus  $I^{\rm co}{}_{\rm Me,CH_2X}$ . Using the values of  $D_{\rm X}$  and  $\sigma$  in a recent compilation,<sup>1b</sup> we have calculated a value of  $C'_{\rm Me_2}$  for each X group listed in Table I. The results are shown in Table II, along with the  $C'_{\rm Me_2}$  values that may be calculated by neglecting the interactions calculated by using eq 9. In this case we obtain eq 11 and use the  $D_{\rm X}$  values

$$\Delta G^{\rm chem} = C'_{\rm Me_2} - D_{\rm X} \tag{11}$$

that were obtained in a least-squares treatment in which polar interactions of substituents across the carbon-carbon double bond were neglected<sup>1b</sup> instead of the  $D_X$  values obtained in a treatment allowing for such interaction,<sup>1b</sup> which were used with eq 10. Table II also contains the  $\Delta G^{\text{chem}}$  values for eq 3 for the various X groups<sup>18</sup> and also values of the difference between  $\Delta G^{\text{chem}}(\text{eq 3})$  and  $\Delta G^{\text{chem}}(\text{eq 2})$ . These values tell how well the equilibrium constants for eq 2 are correlated with those for eq 3.

The average values for  $C'_{Me_2}$  in Table II are well within the combined experimental uncertainties of the value 4.05 kcal/mol that may be calculated from the appropriate group contributions (referring to the gas phase at 25 °C).

Because of the tendency of electrically charged substituents to give deviations from linear free energy relationships, the  $CO_2^-$  substituent was the only substituent involved in several equilibria that was not used in the least-squares treatments from which the value of  $\tau_v$  was obtained.<sup>1b,2</sup> It is not surprising that this substituent gives the largest deviation from each of the three correlations covered by Table II. Hence, the  $CO_2^-$  data were neglected in calculating the average values listed. The values of  $C'_{Me_2}$ and  $\Delta G^{\text{chem}}(\text{eq } 2) - \Delta G^{\text{chem}}(\text{eq } 3)$  are seen to be constant within standard deviations of about the same size as obtained in correlating reactions of the same type as eq 1.<sup>2,18</sup> We conclude that the  $D_X$  values we have obtained are more broadly applicable than just to reactions of the same type as eq 1.

#### **Experimental Section**

**Reagents.** The 5-methyl-3-hexen-2-one (2) available commercially (Aldrich), after distillation, gave only one major peak upon VPC with 6 ft  $\times$  0.25 in. columns with diethylene glycol, diisodecyl phthalate, polyphenyl ether (five ring), or Carbowax 20M or on a 20-ft Apiezon L column. However, the <sup>1</sup>H NMR spectrum showed that about 20% 5-methyl-4-hexen-2-one (1) was present. Gravity chromatography on a 2 ft  $\times$  1.5 in. Florisil column (elution with pentane containing increasing amounts of ether) did not cleanly separate the isomers, but the conjugated isomer tended to be eluted more slowly. From 10.5 g of ketone some of the later fractions gave ~0.5 g of 2 in which no 1 could be seen

<sup>(18)</sup> Hine, J.; Skoglund, M. J. J. Org. Chem. 1982, 47, 4758-66.

## Equilibration of XCH<sub>2</sub>CH=CYZ/XCH=CHCHYZ Pairs

by <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz):  $\delta$  6.78 (dd, 1, J = 16 Hz, J' = 7 Hz, COCH—CH), 6.02 (dd, 1, J = 16 Hz, J' = 1.1 Hz, COCH—C), 2.41 (m, 1, CHMe<sub>2</sub>), 2.22 (s, 3, CH<sub>3</sub>CO), 1.07 [d, 6, J = 6.8 Hz, (CH<sub>3</sub>)<sub>2</sub>CH]; IR (neat) 2970, 2800, 1675, 1625, 1470, 1360, 1260, 985 cm<sup>-1</sup> UV max (methanol) 221 nm ( $\epsilon$  12 400), 306 (30) [lit.<sup>19</sup> IR (C<sub>2</sub>Cl<sub>4</sub>) 1702, 1683, 1626 cm<sup>-1</sup>; lit<sup>20</sup> IR (neat) 1661, 1615, 982 cm<sup>-1</sup>; UV (96% EtOH) 222 nm ( $\epsilon$  13 000), 298 (46)]. As little as 1% of 1 should have been detectable.

Irradiation of four 20-g batches of redistilled commercial 2 under the conditions of Yang and Jorgenson<sup>21</sup> for 12 h gave material in whose <sup>1</sup>H NMR spectrum no clear evidence for the presence of *trans*-2 could be found. Distillation gave (in the early fractions) a yield of 50% 1: bp 55 °C (30 mm); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz)  $\delta$  5.31 (m, 1, CH=C), 3.1 (br d, 2, J = 6 Hz, CH<sub>2</sub>), 2.13 (s, 3, CH<sub>3</sub>CO), 1.76 (br s, 3, CH<sub>3</sub>C=C), 1.66 (br s, 3, CH<sub>3</sub>C=C); IR (neat) 2980, 2920, 1715, 1445, 1380, 1360, 1160 cm<sup>-1</sup>; UV max (methanol) 283 nm ( $\epsilon$  98) [lit.<sup>21</sup> <sup>1</sup>H NMR  $\delta$  5.32 (t, 1, J = 7 Hz), 3.05 (d, 2, J = 7 Hz), 2.06 (s, 3), 1.80 (s, 3), 1.65 (s, 3); lit.<sup>20</sup> bp 76 °C (50 mm); IR (neat) 1700, 1664, 844 cm<sup>-1</sup>; UV (96% EtOH) 283 nm ( $\epsilon$  123)]. We estimate that no more than 4% 2 was present in the 1 thus obtained.

Equilibrations. In a typical equilibration run 10 mL of 4.19 M 1 in t-BuOH and 10 mL of 2.27 M DBU in t-BuOH were mixed and kept at 25 °C. At 8, 24, 33, 54, 78, 102, and 126 h, ~2-mL samples were removed and added to the amount of dilute HCl needed to neutralize the base. The aqueous solution was extracted with three 10-mL portions of ether, which were combined, dried over MgSO<sub>4</sub>, and concentrated to remove almost all the ether. The 90-MHz <sup>1</sup>H NMR spectrum of the residue in CDCl<sub>3</sub> was integrated and relative concentrations were calculated from the areas of the methyl peaks. According to the 8-h point the half-life of the equilibration reaction under the preceding conditions is about 3 h. The data from all the points taken after 9 half-lives (which showed no trend) were averaged. The equilibrium constant (standard deviation) calculated from the size of the acetyl methyl peaks was 0.401 (0.005), and the value from the gem-dimethyl peaks was 0.394 (0.006). When equilibrium was approached by starting with 80% 2-20% 1, values of 0.403 (0.006) and 0.399 (0.006) were obtained. When mixtures of weighed amounts of 1 and 2 were subjected to the workup procedure and analysis, the average results agreed with the known values, but the average deviation from the mean was 8%.

In the runs at  $\sim$ 85 °C, extraneous peaks appeared in the NMR spectra for points taken at 30 h and later. The data from these points were not used.

When equal volumes of 0.96 M 80% 2–20% 1 and 0.25 M t-BuOK, both in Me<sub>2</sub>SO, were mixed at room temperature, the mixture became hot and had become black within 20 min, when it was worked up. The <sup>1</sup>H NMR of the product contained many peaks, but neither 1 nor 2 was clearly present. Neither 0.25 M Et<sub>3</sub>N nor 0.21 M 1.4-diazabicyclo[2.2.2]octane in t-BuOH produced any significant change in the 2/1 ratio over a period of 24 h at 25 °C.

#### Appendix

By use of a correlation of thermodynamic properties in terms of group contributions,<sup>22</sup>  $\Delta G^{\text{chem}}$  for eq 2 may be expressed as shown in eq 12. Since  $D_X$  is defined in eq

$$\Delta G^{\text{chem}} = [CHYZ(C_d)] - [C_dYZ] - [CH_2X(C_d)] + [C_dHX] + I^t_{X,CHYZ} - I^t_{Y,CH_2X} - I^c_{Z,CH_2X}$$
(12)

13, we may change eq 12 to eq 14, from which eq 15 follows.  $D_{X} = [C_{d}H_{2}] + [CH_{2}X(C_{d})] - [CH_{3}(C_{d})] - [C_{d}HX] (13)$   $\Delta G^{chem} = [CHYZ(C_{d})] + [C_{d}H_{2}] - [CH_{3}(C_{d})] - [C_{d}YZ] - D_{x} + P_{X,CHYZ} - P_{Y,CH_{2}X} - P_{Z,CH_{2}X} (14)$   $C_{YZ} = [CHYZ(C_{d})] + [C_{d}H_{2}] - [CH_{3}(C_{d})] - [C_{d}YZ]$ (15)

The cases where Y and Z are both methyl groups give eq 16. The parameter values give a  $\Delta H$  of 4.52 kcal/mol and  $C_{Y} = [CH(C)_{2}(C_{1})] + [C_{1}H_{2}] - [CH_{2}(C_{1})] - [C_{1}(C)_{2}]$ 

$$C_{Me_2} = [CH(C)_2(C_d)] + [C_dH_2] - [CH_3(C_d)] - [C_d(C)_2]$$
(16)

a  $\Delta S_{\rm chem}$  of -1.79 eu, which may be combined to give a  $\Delta G^{\rm chem}(298 {\rm K})$  or  $C_{\rm Me_2}$  value of 5.05 kcal/mol. Subtraction of an  $I^c_{\rm C,CH_2C}$  value of 1.00 kcal/mol gives a value of 4.05 kcal/mol for  $C'_{\rm Me_2}$ .

**Registry No.** 1, 28332-44-7; (*E*)-2, 1821-29-0; CH<sub>3</sub>CH=CMe<sub>2</sub>, 513-35-9; CH<sub>2</sub>=CHCHMe<sub>2</sub>, 563-45-1; MeCH<sub>2</sub>CH=CMe<sub>2</sub>, 625-27-4; (*E*)-MeCH=CHCHMe<sub>2</sub>, 674-76-0; PhCH<sub>2</sub>CH=CMe<sub>2</sub>, 4489-84-3; (*E*)-PhCH=CHCHMe<sub>2</sub>, 15325-61-8; NO<sub>2</sub>CH<sub>2</sub>CH=CMe<sub>2</sub>, 1809-65-0; (*E*)-NO<sub>2</sub>CH=CHCHMe<sub>2</sub>, 27675-38-3;  $^{\circ}O_{2}$ CCH=CHCHMe<sub>2</sub>, 69113-34-4; (*E*)- $^{\circ}O_{2}$ CCH=CHCHMe<sub>2</sub>, 69113-34-4; (*E*)- $^{\circ}O_{2}$ CCH=CHCHMe<sub>2</sub>, 69113-33-3; (*E*)-BuSCH=CHCHMe<sub>2</sub>, 69152-79-0; CO<sub>2</sub>EtCH<sub>2</sub>CHe<sub>2</sub>CMe<sub>2</sub>, 6849-18-9; (*E*)-CO<sub>2</sub>EtCH=CHCHMe<sub>2</sub>, 15790-86-0; CNCH<sub>2</sub>CH=CMe<sub>2</sub>, 4786-23-6; (*E*)-CNCH=CHCHMe<sub>2</sub>, 1119-15-9; DBU, 6674-22-2; 4-hexen-2-one, 25659-22-7; 3-hexen-2-one, 763-93-9.

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