

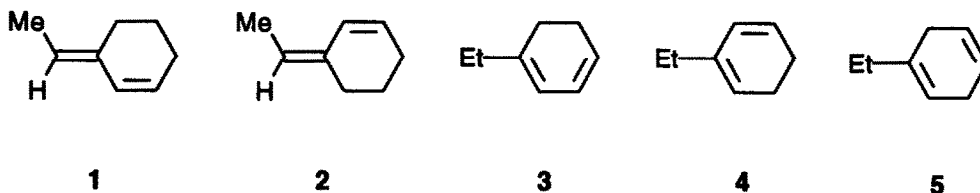
Relative Thermodynamic Stabilities of 3-Ethylidenecyclohexenes and Isomeric Ethylcyclohexadienes

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Abstract: The relative thermodynamic stabilities of the *E* and *Z* forms of 3-ethylidenecyclohexene, 1-ethyl-1,3-cyclohexadiene, 2-ethyl-1,3-cyclohexadiene and 1-ethyl-1,4-cyclohexadiene were determined by *t*-BuOK catalyzed chemical equilibration in DMSO solution. From the variation of the equilibrium composition with temperature the enthalpy, entropy and Gibbs energy differences between the isomeric species were evaluated. The ethylidenecyclohexenes were found to be the most abundant species at thermodynamic equilibrium, owing to their 9–12 kJ mol⁻¹ lower enthalpy values. The entropy term, however, favors the cyclohexadienes by 7–11 J K⁻¹ mol⁻¹.

Potassium *tert*-butoxide in DMSO is a well-known strongly basic reagent, useful for a variety of reactions such as double bond migrations in olefinic compounds. We have previously utilized this property of *t*-BuOK for synthetic purposes in the conversion of allylic ethers,¹ acetals,^{1,2} orthoformates³ and orthocarbonates⁴ into the corresponding propenyl compounds, as well as for establishing a thermodynamic equilibrium between the isomeric allyl and propenyl compounds.⁴ The same reagent was also used for determination of thermodynamic stabilities of isomeric cyclohexadienes, cycloheptadienes and cyclooctadienes.^{5,6} In the present work *t*-BuOK was used to produce a thermodynamic equilibrium between the 12 isomeric conjugated and nonconjugated dienes derived from commercial 4-vinylcyclohexene. (The compounds include 3 vinylcyclohexenes, 4 ethylidenecyclohexenes, and 5 ethylcyclohexadienes). Previously, 4-vinylcyclohexene was subjected to a kinetic isomerization study by Bank *et al.*,⁷ who found that the major isomerization products (though not at a state of thermodynamic equilibrium) were the (*E*)- and (*Z*)-3-ethylidenecyclohexenes 1 and 2. In addition, moderate amounts of the three cyclohexadienes 3–5 were found, together with large amounts of the unchanged reagent.



Since the work of Bank *et al.* was a kinetic, not a thermodynamic one, the reported constitution of the reaction mixture cannot be used to estimate the true thermodynamic stabilities of the isomeric species. To determine the relative Gibbs energy, enthalpy and entropy values of the various isomeric forms, we have now analyzed by GLC the equilibrium compositions of the reaction mixture at numerous temperatures. Though the reaction mixture consists of 12 isomeric species, only 5 of them (1–5) were sufficiently abundant to allow separation for spectral characterization and accurate determination of concentration.

RESULTS AND DISCUSSION

Bank *et al.*⁷ observed that under reaction conditions more severe than those necessary for the isomerization a simultaneous disproportionation reaction takes place, leading to a formation of ethylbenzene and ethylcyclohexenes. This side reaction was clearly discernible in our work, too, but under the experimental conditions used the desired isomerization reaction was the dominating one. The relative equilibrium concentrations of 1–5 at various temperatures are given in Table 1. For the 5 isomeric species included, 10 different isomerization reactions may be presented; Table 1 gives the values of the thermodynamic parameters of isomerization for the most interesting ones of them. These data were obtained by linear least-squares treatment of $\ln K$ vs. T^{-1} according to the van't Hoff equation; here K is the mean equilibrium constant, calculated from the concentration data of Table 1.

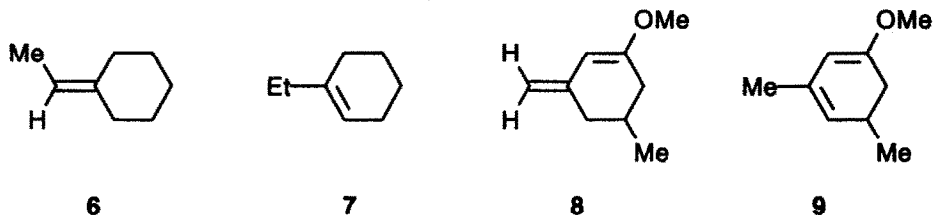
The small stability difference between the geometrical isomers 1 and 2 is expectedly due to the enthalpy term which favors the *E* form (1) by 2.0 kJ mol⁻¹. The lower stability of 2 suggests the *cis* strain between the Me group and the adjacent olefinic hydrogen of 2 to be more severe than that between the Me group and the neighboring ring methylene group of 1. For comparison, the enthalpy difference between 1 and 2 was calculated by the COSMIC⁸ force field: the *E* isomer was predicted to be the more stable compound by 0.8 kJ mol⁻¹, in moderate agreement with the experimental value of 2.0 ± 0.4 kJ mol⁻¹.

Table 1. Relative Equilibrium Concentrations of 1–5 at Various Temperatures, and the Values of ΔG° , ΔH° and ΔS° of Isomerization at 298.15 K. The Errors are Twice the Standard Errors.

$t/^\circ\text{C}$	$c(1)/\%$	$c(2)/\%$	$c(3)/\%$	$c(4)/\%$	$c(5)/\%$
25	59.7	28.8	6.1	1.8	3.6
60	55.5	29.4	7.7	2.8	4.6
80	53.3	30.3	8.2	3.3	4.9
100	51.0	28.6	10.2	4.0	6.2
130	47.3	28.2	12.3	4.9	7.4
150	45.0	27.7	13.5	5.8	8.0

Reaction	$\Delta G^\circ/\text{kJ mol}^{-1}$	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\Delta S^\circ/\text{J K}^{-1} \text{mol}^{-1}$
1 \rightarrow 2	1.79 ± 0.08	2.0 ± 0.4	0.6 ± 1.1
1 \rightarrow 3	5.81 ± 0.28	9.2 ± 1.4	11 ± 4
1 \rightarrow 4	8.70 ± 0.10	12.0 ± 0.5	11.1 ± 1.4
1 \rightarrow 5	7.10 ± 0.26	9.3 ± 1.3	7 ± 4
3 \rightarrow 4	2.89 ± 0.23	2.8 ± 1.2	0 ± 3
3 \rightarrow 5	1.29 ± 0.04	0.1 ± 0.2	-4.0 ± 0.6
4 \rightarrow 5	-1.60 ± 0.23	-2.7 ± 1.2	-4 ± 3

Table 1 shows that the higher stability of the 3-ethylidenecyclohexenes at equilibrium arises from their lower enthalpy values. The entropy term, however, favors the ethylcyclohexadienes 3–5 by 7–11 $\text{J K}^{-1} \text{mol}^{-1}$. The isomerization of 1 to 4 is formally related to that of ethylidenecyclohexane (6) to 1-ethylcyclohexene (7). Energetically, however, these reactions are far from each other: the former is endothermic by 12.0 kJ mol^{-1} , but the latter exothermic by 5.0 kJ mol^{-1} in acetic acid solution.⁹ Since, on going from 1 to 4, the 1,3-diene system is maintained, whereas both 6 and 7 have a single C=C bond, the difference of 17 kJ mol^{-1} between the reaction enthalpies reveals the previously documented¹⁰ (but poorly understood) weak stability of the 1,3-cyclohexadiene ring system.



Reaction **1** \rightarrow **4** is also related to reaction **8** \rightarrow **9**, for which $\Delta H^\circ = 4.6 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = 9.9 \text{ J K}^{-1} \text{ mol}^{-1}$.⁶ In both reactions, the entropy changes are similar, but the former reaction is more endothermic by 7 kJ mol^{-1} . This difference in ΔH° is understandable in view of the structural differences between **1** and **8**. Firstly, the exocyclic C=C bond of **1** is stabilized over that of **8** by a Me group. On the other hand, however, the same Me group causes a destabilizing *cis* interaction with the neighboring ring hydrogens. If the double-bond stabilization energy of the Me group in **1** is taken as 11 kJ mol^{-1} , the value normally found in olefinic compounds,¹¹ the steric interaction of the Me group with the ring hydrogens of **1** is calculated to be $11 - 7 = 4 \text{ kJ mol}^{-1}$. This is in line with the respective *cis* interaction energies in (*Z*)-2-butene¹² and (*Z*)-2-pentene.¹³

Among the three cyclohexadienes **3**–**5**, the 2-Et derivative has the lowest and the 1-Et derivative the highest thermodynamic stability. This order of thermodynamic stability agrees with that observed previously for related alkoxy-substituted cyclohexadienes.⁶ Considering the isomerization of 1-R-1,4-cyclohexadiene to 1-R-1,3-cyclohexadiene, the values of ΔH° are 1.6, -0.1 and -2.1 kJ mol^{-1} for R = H,⁶ Et (this work) and MeO,⁶ respectively. On the other hand, the respective reaction enthalpies are 1.6, 2.7 and 7.0 kJ mol^{-1} for the reaction 1-R-1,4-cyclohexadiene \rightarrow 2-R-1,3-cyclohexadiene. Thus the electron donating Et and MeO groups at the 1-position increase but at the 2-position decrease the relative thermodynamic stability of the 1,3-cyclohexadiene, in comparison with that of 1-R-1,4-cyclohexadiene. In particular, the presence of a MeO substituent at the 2-position has a marked destabilizing effect on 1,3-cyclohexadiene, for no obvious reason.

EXPERIMENTAL*Materials.*

Commercial 4-vinylcyclohexene was treated with *t*-BuOK in DMSO to get an approximately equilibrium mixture of the isomeric forms. The crude mixture of isomers obtained was then distilled on a Perkin-Elmer M251 Auto Annular Still into fractions for spectral characterization and the equilibration experiments. The compounds were identified by their ^{13}C NMR spectra; however, the configurational assignments of **1** and **2** were aided by ^1H NMR spectroscopy: the olefinic ring hydrogen at C-2 of **1** has a characteristic ^1H NMR absorption at δ 6.29 and that of **2** at δ 5.89.¹⁴ This assignment agrees with evidence given by the ^{13}C NMR data: due to the γ effect of the Me group, the C-2 atom of **2** is found 7.0 ppm upfield from that of **1**. Correspondingly, C-4 of **1** was shielded by 7.2 ppm relative to that of **2**.

^{13}C NMR (CDCl_3). **1**: 121.0 (C-1), 131.2 (C-2), 134.2 (C-3), 25.0 (C-4), 22.6 (C-5), 25.7 (C-6), 126.7 (CH), 12.9 (CH_3). **2**: 119.2 (C-1), 124.2 (C-2), 135.7 (C-3), 32.4 (C-4), 23.4 (C-5), 26.3 (C-6), 129.2 (CH), 12.4 (CH_3). **3**: 141.6 (C-1), 117.4 (C-2), 124.9 (C-3), 123.4 (C-4), 23.1 (C-5), 26.7 (C-6), 30.2 (CH_2), 12.1 (CH_3). **4**: 118.8 (C-1), 137.5 (C-2), 127.4 (C-3), 126.5 (C-4), 22.6 (C-5), 22.5 (C-6), 28.4 (CH_2), 12.8 (CH_3). **5**: 136.7 (C-1), 117.0 (C-2), 26.9 (C-3), 124.5 (C-4), 124.7 (C-5), 29.1 (C-6), 30.2 (CH_2), 12.0 (CH_3).

Equilibrations.

Since the extent of the disturbing disproportionation reaction increases with increasing reaction time, the latter was made as short as possible by using for the equilibration experiments mixtures of isomers that were close to the equilibrium concentrations. Substrate and catalyst (*t*-BuOK) concentrations were maintained at 20 % (v/v) and 10-15 % (m/v), respectively, in dry DMSO. The equilibrated samples were analyzed by GLC using a 25 m XE-60 capillary column and a 4 m Carbowax 20M packed column (two columns were required since the peaks of **3** and **5** were not resolved in the XE-60 column). More experimental details are given in Ref. 5.

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