Simple Enols. 5.[1] (Z)- and (E)-1-Hydroxy-1,3-butadiene

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Abstract: (Z)- and (E)-1-hydroxybutadiene have been generated from their trimethylsilyl derivatives in slightly acidic aqueous acetonitrile and CH_3OH–DMSO mixtures and characterized by NMR spectroscopy. The kinetics and products of ketonization of both dienols have been investigated. In aqueous solution they yield mixtures of (E)-2-butenal and 3-butenal whose proportions depend on pH. Analysis of the variation of product composition with pH indicates that (E)-1-hydroxybutadiene yields 90.1, 28.0, and 44.7% of (E)-2-butenal in the H_3O^+, H_2O, and HO^--catalyzed reactions, whereas (Z)-1-hydroxybutadiene yields 69.8, 17.2, and 19.6%. It is suggested that transmission of positive charge to the oxygen in the transition state for protonation at the 4-position is more efficient with the E than with the Z isomer, possibly because it is easier for the former to attain a planar conformation. No evidence was found for a mechanism that involves a cyclic transition state for the spontaneous ketonization of (Z)-butadienol.

(Z)- and (E)-1-hydroxy-1,3-butadiene are the simplest 1,3-dienols, a class of compounds whose members and their anions have frequently been postulated as intermediates in thermal[2-9] and photochemical[10,11] reactions. 1-Hydroxy-1,3-butadiene itself was postulated as an intermediate in the gas-phase photoisomerization of crotonaldehyde into 3-buten-1-al[12] and tentatively assigned as one of the products of the gas-phase photolysis of crotonaldehyde on the basis of its IR spectrum (ν = 3630, 1100 cm^{-1}).[13] Recently Tureček and co-workers have reported the generation of the Z and E isomers in the gas phase by retro-Diels–Alder reactions at 750 °C of their adducts with cyclopentadiene.[14] The dienols, mixed with not more than 10–15% crotonaldehyde, were characterized by mass spectrometry, on the assumption that molecular geometry was conserved in the pyrolyses reactions. This paper reports the first investigation of the 1-hydroxy-1,3-butadienes in solution.

Results and Discussion

Generation and Characterization of (Z)- and (E)-1-Hydroxy-1,3-butadiene. Simple enols, e.g., vinyl alcohol, may be generated in solution by controlled hydrolysis under slightly acidic conditions of their protected forms with ketene acetals or ortho esters as the protective groups.[1,15-19] Heterocyclic enols derived from furan and thiophene and their benzo derivatives which are more stable may be generated similarly, but now the less-reactive trimethylsilyl derivatives can be used as these can be deprotected faster than the enols ketonize.[19] As it seemed likely that the hydroxybutadienes would ketonize more slowly than vinyl alcohol, it was thought that their trimethylsilyl derivatives should also be suitable precursors for these dienols. The Z[20] and E[21] forms were hydrolyzed separately in CD_3CN:D_2O (9:1 v/v) which contained DCl (3.16×10^{-3} M) at 32 °C. The ^1H NMR spectral changes indicated in Scheme I took place. With both isomers after 1 h the signal of the trimethylsilyl group at δ ca. 0.2 had disappeared completely and been replaced by a signal at δ 0.03 ascribed to trimethylsilanol (or hexamethyldisiloxane).[22] Only relatively small changes had occurred in the remainder of the two spectra. With the Z isomer the largest change was an upfield shift of 5.21 to 4.98 ppm of H-2. This is similar to what is found when vinyl alcohol and the heterocyclic enols studied previously are liberated from their protected forms. There were also smaller upfield shifts of about 0.06 ppm of the δ protons H-4 and H-5. With the E isomer the upfield shift of H-2 was similar, 5.67 to 5.53, but the

Scheme I. ^1H NMR Spectral Changes (δ Values) on Hydrolysis of 1-(Trimethylsilyloxy)-1,3-butadienes in CD_3CN:D_2O (9:1 v/v) that Contains DCl (3.16×10^{-3} M) at 32 °C

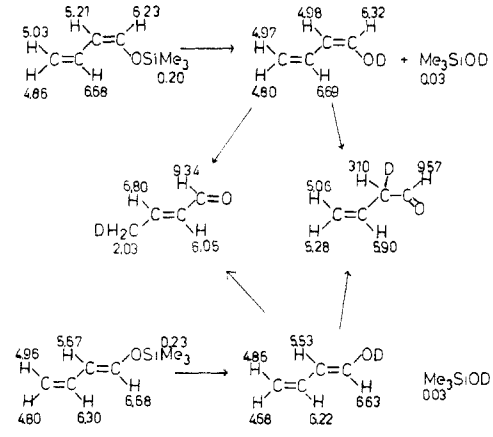

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Table I. Rate Constants and Products of the Ketonization of (*Z*)- and (*E*)-Hydroxybutadiene in Water (I = 1.0 M) at 25 °C

	Z isomer		*E* isomer	
catalyst	rate constant (esd)	fraction of (*E*)-2-butenal (esd)	rate constant (esd)	praction of (*E*)-2-butenal (esd)
H_3O^+	9.55×10^{-2} (2×10^{-3}) M^{-1} s^{-1}	0.698 (0.007)	0.530 (0.013) M^{-1} s^{-1}	0.901 (0.013)
H_2O	3.99×10^{-3} (9×10^{-5}) s^{-1}	0.172 (0.008)	3.03×10^{-3} (1.6×10^{-4}) s^{-1}	0.280 (0.017)
HO^-	1.28×10^5 (2.5×10^3) M^{-1} s^{-1}	0.196 (0.017)	1.14×10^5 (4×10^3) M^{-1} s^{-1}	0.447 (0.031)

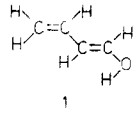
Table II. Rate Constants for Ketonization for Hydroxybutadienes through Protonation at the 2- and 4-Positions in Water (I = 1.0 M) at 25 °C

	Z isomer		*E* isomer	
	2-position	4-position	2-position	4-position
k_{H^+}/M^{-1} s^{-1}	2.88×10^{-2}	6.66×10^{-2}	0.05	0.48
k_{H_2O}/s^{-1}	3.30×10^{-3}	6.9×10^{-4}	2.18×10^{-3}	8.5×10^{-4}
k_{HO^-}/M^{-1} s^{-1}	1.03×10^5	2.5×10^4	6.30×10^4	5.1×10^4

shift of the δ protons was larrger (0.10–0.12). This may arise from the *E* isomer being more nearly planar and the conjugation of the diene system being more highly developed. The signal of H-3 of the (*Z*)-dienol lies at the lower field (δ 6.69) than that of H(1) (δ 6.32). This is similar to what was reported for the alkoxybutadienes[21,23,24] and ascribed to the closeness of H-3 to the electronegative oxygen. It is assumed that the stable conformation of both dienols is s-trans around the C-2–C-3 bond. This is the stable conformation of butadiene[25,26] and of alkoxybutadienes.[24,27] The coupling constant J_{2-3} in the ^1H NMR spectra of both dienols is 10–11 Hz, similar to that reported for the latter compounds.[24] The dienols were stable in the solutions in which they were generated at 25 °C for 2 to 3 days but were slowly converted into a mixture of 3-butenal and (*E*)-2-butenal.

The OH dienols could be generated under conditions of slow exchange in a mixture of DMSO-d_6 and CH_3OH (90:10 v/v) at 32 °C. The signals of the oxygen-bound protons were doublets with δ ca. 8.91 and the signals of the protons attached to C-1 were four-line signals. The HO–C_1–H coupling constants for the *E* and *Z* isomer were respectively 8.8 and 5.8 Hz. This is similar to what is found for (*E*)- and (*Z*)-1-propenols[18] and suggests that the *E* isomer is predominently in the s-cis conformation and the *Z* isomer predominently in the s-trans conformation around the C–O bond.

The predominent conformations of the dienols are therefore as shown in **1** and **2**.



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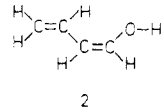

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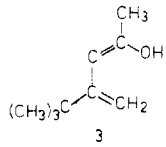

3

Products and Kinetics of Ketonization of (*Z*)- and (*E*)-1-Hydroxy-1,3-butadiene. Ketonization may occur with protonation on C-2 to yield 3-butenal or on C-4 to yield (*Z*)- and (*E*)-2-butenal. Examination of the ^1H NMR spectrum of the kinetically controlled product of the ketonization of both (*E*)- and (*Z*)-dienol in CD_3CN:D_2O (9:1)–DCl (10^{-4} M) indicated the presence of only

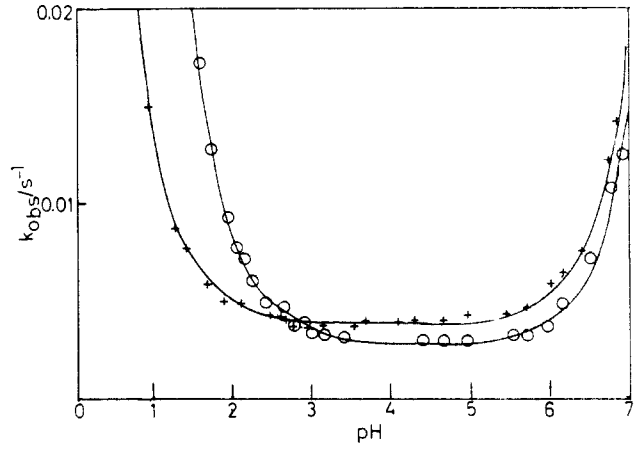

Figure 1. pH–rate profiles for the ketonization of (*E*)- and (*Z*)-1-hydroxy-1,3-butadiene. The circles (*E* isomer) and crosses (*Z* isomer) are the experimental points and the lines are drawn according to eq 1 by using the parameters of Table I. Full data are given in Tables S1 and S2.

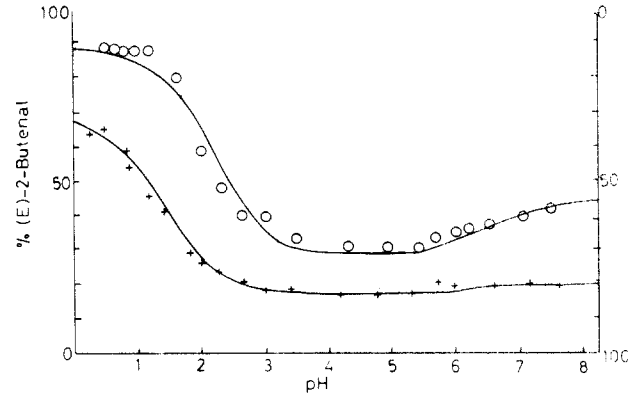

Figure 2. pH–product profiles for the ketonization of (*E*)- and (*Z*)-1-hydroxy-1,3-butadiene. The circles (*E* isomer) and crosses (*Z* isomer) are the experimental points and the lines are drawn by making use of eq 2 and the parameters listed in Table I. Full data are given in Tables S3 and S4.

3-butenal and (*E*)-2-butenal. No (*Z*)-2-butenal, whose proton at C-1 has a chemical shift ca. 0.6 ppm lower than that of the *E* isomer,[28] could be detected. The fractions of 2-butenal and (*E*)-3-butenal in the product and the overall first-order rate constants, k_{obsd}, depend on pH as shown in Figures 1 and 2. The variation of k_{obsd} with pH was fitted to eq 1 and the parameters k_{H^+}, k_{HO^-}, and K_{H_2O} given in Table I were evaluated by a generalized least-squares method.[29] The variation with pH of the fraction of (*E*)-2-butenal in the product, F_{obsd} was fitted to eq 2.

$$k_{obsd} = k_{H^+} \times 10^{-pH} + k_{H_2O} + k_{HO^-} \times K_w/10^{-pH} \quad (1)$$

The values of k_{H^+}, k_{H_2O}, k_{HO^-} (obtained as indicated above), k_{obsd}, and K_w were taken as constants and the parameters F_{H^+}, F_{H_2O},

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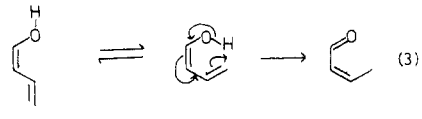
$$F_{obsd} = F_{H^+}\frac{k_{H^+}}{k_{obsd}} \times 10^{-pH} + F_{H_2O}\frac{k_{H_2O}}{k_{obsd}} + F_{HO^-}\frac{k_{HO^-}}{k_{obsd}}K_w/10^{-pH} \quad (2)$$

and F_{HO^-}, the fractions of (*E*)-2-butenal in the product formed in the H^+, H_2O, and HO^--catalyzed reactions, were evaluated by the generalized least-squares procedure.[29] These values are also given in Table I, and the values for the site-specific rate constants for ketonization with protonation at positions 2 and 4 are given in Table II. Both enols undergo H_3O^+-catalyzed ketonization with predominant protonation at γ-position. This is qualitatively similar to what is found on hydrolysis of 1-alkoxy-1,3-butadienes.[31,32] Thus under our conditions (Table I) (*E*)- and (*Z*)-1-hydroxybutadiene react with 90.1 and 69.8% protonation at the γ-position compared to 100 and 78% found on hydrolysis of (*E*)- and (*Z*)-1-ethoxy-1,3-butadiene in 80% aqueous dioxane.[31]

The ketonization of the dienols with protonation at C-2 is analogous to the ketonization of vinyl alcohol for which k_{H^+} = 45.9 M^{-1} s^{-1} (I = 1.0) at 25 °C.[17,30] The additional double bond in the dienols therefore causes a rate decrease of 1544-fold with the *Z* isomer and 918 with the *E* isomer. Ketonization with protonation at the 4-position is 7.3 times faster with the *E* isomer than with the *Z* isomer. This factor is a little less than the factor of 18 that can be calculated for the relative rates of protonation of the corresponding (*E*)- and (*Z*)-butadienyl ethyl ethers in 80% aqueous dioxane from the results of Okuyama and his co-workers.[31] It seems that the transmission of positive charge to the oxygen in the transition state for protonation at the 4-position is more efficient with the *E* than with the *Z* isomers possibly because it is easier for the former to attain a planar conformation. This greater reactivity at the 4-position of the *E* isomer is also shown in the water and hydroxide ion catalyzed reactions of the dienols. The latter presumably involves protonation of the dienolate ions, and as discussed by Whalen and his co-workers[9] the relative rates of protonation will depend on the dihedral angle between the double bonds. The position of protonation of dienolate anions has traditionally been discussed in terms of the charge density at the α- and γ-positions on the assumption that the transition state is early.[3,4] With many dienolate ions derived from steroids and from other six- and eight-membered ring systems there is a strong preference for protonation at the α-position, but, as pointed out by Whalen,[9] when the dienolate system is planar this preference is relatively slight. Thus k_α/k_γ for protonation of the cyclopentadienolate ion[9] is ca. 3 whereas for the cyclohexadienolate ion[9] it is ca. 575 and for the cyclooctadienolate ion[4] it is greater than 1400. As the ratio $k^\alpha_{HO^-}/k^\gamma_{HO^-}$ for the (*E*)- and (*Z*)-dienols is respectively 1.2 and 4.1 it seems that the corresponding dienolate ions probably resemble the cyclopentadienolate ion, presumably because they are almost planar. This difference in behavior is also found in the water-catalyzed or spontaneous reaction as the *Z* and *E* isomers undergo respectively 17.3 and 28% protonation at the α-position whereas 1,3-cyclohexadienol undergoes exclusive γ-protonation.[33]

There is an additional pathway available for the spontaneous ketonization of the (*Z*)-butadienol which is not available for the (*E*)-butadienol nor for monoenols, eq 3. This is similar to that


(3)

proposed for the ketonization of the products of photoenolization[34] and has recently been proposed for the ketonization of the photochemically generated dienol **3**.[11] If this pathway were followed in the spontaneous ketonization of (*Z*)-1-hydroxy-1,3-butadiene it would be expected that (i) the overall proportion of 2-butenal would be higher than that formed from its *E* isomer, (ii) a substantial portion of the 2-butenal formed from (*Z*)-1-hydroxy-1,3-butadiene should be the *Z* isomer, and (iii) the spontaneous ketonization of (*Z*)-1-hydroxy-1,3-butadiene to form 2-butenal should be much faster than that of its *E* isomer. In fact the overall proportion of 2-butenal formed in the spontaneous ketonization of (*Z*)-1-hydroxy-1,3-butadiene is less than that formed from its *E* isomer (see Table I, Figure 2), no (*Z*)-2-butenal could be detected, and the spontaneous ketonization of (*Z*)-1-hydroxy-1,3-butadiene to form 2-butenal is only slightly greater than that of its *E* isomer. It is therefore concluded that, *in this instance*, the pathway of eq 3 is not important.

Experimental Section

(*Z*)-1-(Trimethylsilyloxy)-1,3-butadiene. This was prepared by cleavage of 2,5-dihydrofuran with butyllithium[35] followed by reaction with trimethylsilyl chloride:[20] bp 130–132 °C; NMR (CD_3COCD_3) δ 6.23 (d, 1, J = 6 Hz, =C*H*O–), 6.68 (m, 1, H_2C=C*H*–), 5.21 (q, 1, $J_{1,2}$ = 6 Hz, $J_{2,3}$ = 11 Hz, –C*H*=CHO–), 5.03 (q, 1, $J_{3,4}$ = 17 Hz, $J_{4,5}$ = 2.5 Hz, trans H_2C=CH–), 4.86 (q, 1, $J_{3,5}$ = 11 Hz, $J_{4,5}$ = 2.5 Hz, cis H_2C=CH–), and 0.2 (s, 9).

(*E*)-1-(Trimethylsilyloxy)-1,3-butadiene. The commercial product (Aldrich) which consisted of approximately 85% *E* isomer and 15% *Z* isomer was fractionally distilled several times to yield the *E* isomer greater than 98% pure (NMR):[21] bp 130–131 °C [lit.[36] bp 57–60 °C (50 mmHg)]; NMR (CD_3CN) δ 6.68 (d, 1, =C*H*O–, J =11.5 Hz), 6.30 (m, 1, H_2C=C*H*–), 5.67 (q, 1, $J_{1,2}$ = 11.5 Hz, $J_{2,3}$ = 10 Hz, C*H*CHO–), 4.96 (q, 1, $J_{3,4}$ = 17 Hz, $J_{4,5}$ = 2 Hz, trans H_2C=CH–), 4.80 (q, 1, $J_{3,5}$ = 10 Hz, $J_{4,5}$ = 2 Hz, cis H_2C=CH–), and 0.23 (s, 9).

3-Butenal. 4,4-Diethoxy-1-butene[37] was carefully hydrolyzed with aqueous hydrochloric acid (2%) at 5–10 °C for 3 to 5 h. The product was extracted with ether, washed ($NaHCO_3$), dried ($MgSO_4$), and distilled: bp 102–103 °C (lit.[38] bp 102–103 °C); NMR ($CDCl_3$) δ 3.1 (q, 2, J_{12} = 1.5 Hz, $J_{2,3}$ = 7 Hz, CH_2), 5.28 (m, 1, trans H_2CCH), 5.06 (m, 1, cis H_2CCH), 5.90 (m, 1, H_2CC*H*), and 9.57 (t, 1, $J_{1,2}$ = 1.5 Hz, C*H*O).

(*E*)-2-Butenal. A mixture of 4,4-diethoxy-1-butene (15 g)[37] and 10% hydrochloric acid (100 mL) was heated under reflux for 1.5 h. After cooling, the mixture was extracted with dichlormethane, washed (aqueous $NaHCO_3$), dried ($MgSO_4$), and distilled: bp 102–103 °C (lit.[38] bp 102.2 °C); NMR ($CDCl_3$) δ 2.03 (q, 3, $J_{3,4}$ = 6 Hz, $J_{2,4}$ = 1.5 Hz CH_3CH=), 6.05 (m, 1, =C*H*CHO), 6.80 (m, 1, CH_3*H*C=), and 9.34 (d, 1, $J_{1,2}$ = 8 Hz).

Determination of Rate Constants and Product Composition. First-order rate constants were determined by following the disappearance of the dienols by UV spectrophotometry at a wavelength of 237 nm with a Shimadzu UV-250 spectrophotometer. Eighty values of the absorbance were collected at convenient time intervals with an Apple II microcomputer or Hewlett Packard microcomputer operating "on-line" with the spectrophotometer through a IEEE interface. The reaction was normally followed to greater than 90% completion, and the rate constants were calculated with a generalized least-squares method.[29] The proportions of 3-butenal and (*E*)-2-butenal in the product were determined by following the reaction at 220 nm at which wavelength (*E*)-2-butenal has a strong absorbance (log ε = 4.1) and 3-butenal has zero absorbance. The infinity absorbance was recorded and the pH was then adjusted to pH 11 at which pH 3-butenal is converted rapidly into (*E*)-2-butenal. The fraction of (*E*)-3-butenal in the kinetically controlled product of ketonization of the dienols was calculated from the infinity absorbance at 220 nm and the absorbance after the pH was adjusted to pH 11.

The pHs of all solutions were measured with a Digi-Sense digital pH meter or an Orion Model 231 pH meter with a combined glass–calomel electrode which was standardized with commercial standard buffers (EIL, England) at pH 4.00, 7.00, and 9.19 at 25 °C.

NMR Spectra. ^{1}H NMR spectra were measured on a Varian EM360 spectrometer. The O-deuteriated dienols were generated by adding 10% (v/v) D_2O–DCl (3.16×10^{-3} M) to a solution of their trimethylsilyl derivatives in CD_3CN at probe temperature (32 °C). Hydrolysis took about 1 h and the dienols were stable for 2–3 days at room temperature (25 °C). The OH dienols were generated under conditions of slow exchange by adding CH_3OH (10% v/v) to a solution of the trimethylsilyl

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derivatives in DMSO-d_6 at probe temperature. Methanolysis required 3–4 h under these conditions and the signals of the OH groups of the dienols were doublets with δ ca. 8.9 and those H-1 were quartets instead of doublets as found with the O-deuteriated dienols.

Registry No. 1, 70411-98-2; **2**, 70415-58-6; (*Z*)-1-(trimethylsilyloxy)-1,3-butadiene, 35694-19-0; (*E*)-1-(trimethylsilyloxy)-1,3-butadiene, 35694-20-3.

Supplementary Material Available: Tables S1–4 of rate and product data (4 pages). Ordering information is given on any current masthead page.

Shape-Specific Weak Interactions Related to a Phenyl Group: Determination of Their Enthalpies by Gas–Liquid Partition Chromatography

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Abstract: When gas chromatography is used, the enthalpies of the interactions between a phenyl group and a variety of sample molecules (alkanes, alkenes, substituted benzenes, ethers, and carbonyl compounds) are evaluated with the uncertainty mostly lower than ±0.04 kcal mol^{-1}. The $\Delta\Delta H^{\circ}$, a measure of the interaction of a phenyl group in a stationary liquid with a given sample, ranges from −2.7 to +0.1 kcal mol^{-1}. It is found that the interaction of a phenyl group is (i) specific for the three-dimensional shape of the sample molecule and (ii) more attractive with a cyclic molecule, which in three-dimensional shape is similar to the phenyl group, than with the corresponding acyclic molecule. The relation of the shape-specific weak interactions presented here to the charge-transfer interaction, π-electron interactions, dipole–induced-dipole interaction, and so on, is discussed.

There is now much evidence for the existence of weak attractive interactions associated with a phenyl group. These include alkyl–phenyl interactions,[1] a dipole–induced-dipole interaction[2] between the 1,3-dioxane and phenyl rings, aromatic–aromatic interactions[3] between the aromatic side chains in model peptides and proteins, "carbonyl–aromatic interactions"[4] in proteins, and amino–aromatic interactions[5] in proteins. These interactions[1-5] are shown to affect molecular conformations and chemical selectivity.[6,8] Little is known, however, about the *enthalpies* and *specificity* of these weak interactions, which aid a better understanding of the high specificity of molecular recognition in chemical as well as biochemical reactions.

In gas–liquid partition chromatography (GLPC), weak interactions between sample molecules and a stationary phase as well as heat of vaporization of samples play a significant role in the separation of samples.[9] This led us to explore a novel method for determining the interaction enthalpies by using GLPC. We report here the full details of studies on the enthalpies of shape-specific weak interactions of a phenyl group with a wide variety of sample molecules including alkanes,[10a] alkenes,[10b] ethers,[10b] substituted benzenes,[10c] and carbonyl compounds.

Results and Discussion

Evaluation of Interaction Enthalpies. A pair of stationary liquids (**1** and **2**; Chart I) was employed for the determination of retention time. The ratio of the retention time for a given sample (**4–11**) to that for the standard one [*n*-octane (**3**)][11] was defined as the relative retention (α). The ln α is related to the free energy changes for solution (ΔG) of samples in a given stationary liquid (liquid A)[12] (eq 1) where $\Delta\Delta G^{(A)}$ represents the differences in

$$-RT \ln \alpha = \Delta G(\mathbf{4}) - \Delta G(\mathbf{3}) = \Delta\Delta G^{(A)} \quad (1)$$

ΔG between samples **4–11** and **3**. Equation 1 can be expressed as[13] eq 2 and 3 where $\Delta\Delta H^{(A)}$ refers to the difference in heat of

$$\ln \alpha = -\Delta\Delta H^{(A)}/RT + \text{constant} \quad (2)$$

$$\Delta\Delta H^{(A)} = \Delta H^{(A)}(\mathbf{4}) - \Delta H^{(A)}(\mathbf{3}) \quad (3)$$

solution in liquid A ($\Delta H^{(A)}$) between samples **4–11** and **3**. As might be expected from eq 2, plots of ln α against T^{-1} give a

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