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STRUCTURE AND REACTIVITY OF α,β-UNSATURATED ETHERS—IX

THE *cis–trans* ISOMERIZATION EQUILIBRIA IN THE LIQUID PHASE

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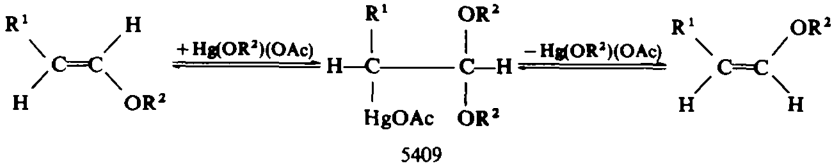
Abstract—The relative stability of various pairs of *cis*- and *trans*-α,β-unsaturated ethers has been determined by geometrical isomerization equilibrium experiments. The isomerization was carried out in bulk in the presence of mercuric acetate at 20 to 50°. The *trans* isomers of alkenyl and styryl ethyl ethers generally are thermochemically more stable than the corresponding *cis* ethers by 0·4 to 1·7 kcal/mole. In the case of propenyl alkyl ethers, the methyl, ethyl, and isobutyl ethers are more stable in the *trans* form, whereas the reverse is true for both the isopropyl and t-butyl ethers. In all these cases, the entropy term favours the stability of the *cis* ethers. These facts are probably due to the rotational isomerism around the sp^2 C—O bond. *cis*-β-Chlorovinyl and *cis*-β-ethoxyvinyl ethyl ethers were found to be more stable than the *trans* isomers.

INTRODUCTION

IN PREVIOUS papers,[1-6] we investigated the rates and mechanisms of acid-catalyzed reactions of various α,β-unsaturated ethers with particular attention to the effects of their geometrical structure. Silver-ion complexation of *cis* and *trans* ethers was also investigated.[7,8] Most of the *cis* ethers show greater reactivity than the corresponding *trans* isomers. The relative stability of geometrical isomers, which may indicate the origin of their relative reactivity, can be directly measured by the isomerization equilibrium experiments.

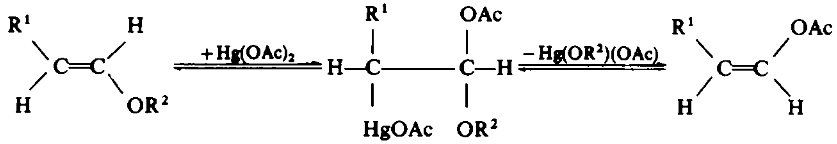
The quantitative investigations on the relative stability of geometrical isomers have been limited to certain alkenes,[9] and in the case of some polar olefins the results are no more than qualitative.[10]

The present communication reports the equilibrium data for the mutual isomerization of various *cis*- and *trans*-α,β-unsaturated ethers in the liquid phase at ordinary temperature. It has been found that *cis*- and *trans*-β-substituted vinyl ethers undergo the geometrical isomerization in bulk to attain equilibrium in the presence of mercuric acetate, a catalyst for the alcohol exchange of vinyl ethers.[11] The isomerization seems to take place through the reversible oxymercuration and deoxymercuration:



(1)

The alkoxymercuric acetate, $Hg(OR^2)(OAc)$, probably being formed by the following reactions,



(2)

which do not seriously perturb the equilibrium in question.

RESULTS

Fig. 1 illustrates a typical course of the geometrical isomerization. The molar fraction of *cis*-1-butenyl ethyl ether, which was attained after sufficiently prolonged reaction times, was independent of the starting isomer composition. Usually, the equilibrium was reached within 20 hr from any isomeric mixtures of the ethers investigated.

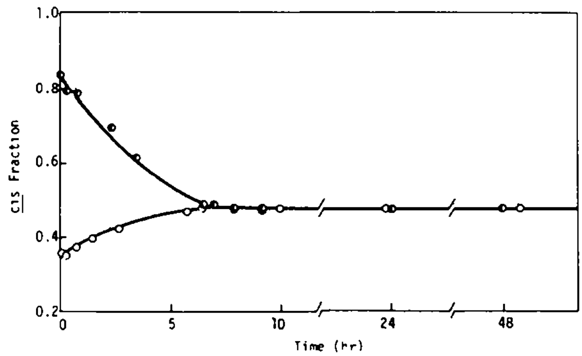


FIG. 1 Variation of the *cis–trans* isomeric composition in the isomerization of 1-butenyl ethyl ether at 25°.

Table 1 presents the equilibrium isomer compositions of 1-butenyl and β-chlorovinyl ethyl ethers studied with different isomer compositions at various temperatures between 25 and 50°. Table 1 also indicates that the total amounts of the *cis* and *trans* ethers remained practically invariant during the course of isomerization. Evaluation of the equilibrium constants, K, was based on these

$$K = [cis]_e/[trans]_e = \exp(\Delta S^\circ/R)\exp(-\Delta H^\circ/RT) \tag{3}$$

In Table 2 are listed the equilibrium constants, K, obtained for various ethers at 25°, together with the enthalpy and entropy changes, ΔH° and ΔS°, accompanying the isomerization. Both the ΔH° and ΔS° were computed from the least-squares treatments of the van't Hoff plots of ten to fifteen K-values measured independently at temperatures from 20 to 50°. Fig. 2 shows the plots for 1-butenyl and β-chlorovinyl ethyl ethers.

DISCUSSION

Effects of the β-substituents. In the first place, we have examined the influence of β-substituents (R^1) on the relative stabilities of *cis* and *trans* isomers of β-substituted

TABLE 1. EXAMPLES OF ISOMERIZATION DATA FOR α,β-UNSATURATED ETHERS

Temp (°C)	$\frac{[cis]_0}{[trans]_0}$	$\frac{[cis]_e}{[trans]_e}$	$\frac{[cis]_e + [trans]_e}{[cis]_0 + [trans]_0}$
	$C_2H_5CH{=}CHOC_2H_5$		
25	2·418	0·869	0·99
25	0·565	0·849	0·93
25	2·418	0·877	0·98
25	0·606	0·888	0·99
30	5·148	0·899	0·97
30	0·576	0·896	0·96
40	0·940	0·898	0·89
40	2·418	0·919	0·99
40	0·606	0·924	0·98
50	5·148	0·938	0·95
50	0·576	0·943	0·96
	$ClCH{=}CHOC_2H_5$		
25	3·900	4·528	0·99
25	4·675	4·640	0·99
30	1·560	4·492	0·90
30	7·960	4·289	0·95
40	4·713	4·342	0·98
40	3·702	4·216	0·96
40	3·634	4·203	0·98
50	1·560	4·030	0·95
50	3·509	4·275	1·00
50	3·837	4·170	1·00
50	5·139	4·202	0·99

TABLE 2. THE EQUILIBRIUM CONSTANTS, K, AND THE ENTHALPY AND ENTROPY CHANGES, $\Delta H°$ AND $\Delta S°$, FOR THE *cis-trans* ISOMERIZATIONS OF SEVERAL α,β-UNSATURATED ETHERS, $R^1CH{=}CHOR^2$

No.	R^1	R^2	K at 25°	$\Delta H°$,[a] kcal/mole	$\Delta S°$,[a] e.u.	Internal standard
1	CH_3	C_2H_5	1·385	$0{\cdot}37_2 \pm 0{\cdot}02_8$	$1{\cdot}8_9 \pm 0{\cdot}1_4$	*n*-hexane
2	C_2H_5	C_2H_5	0·874	$0{\cdot}56_5 \pm 0{\cdot}08_9$	$1{\cdot}6_3 \pm 0{\cdot}2_9$	*n*-heptane
3	$i\text{-}C_3H_7$	C_2H_5	0·583	$0{\cdot}78_4 \pm 0{\cdot}06_4$	$1{\cdot}5_6 \pm 0{\cdot}2_0$	*n*-octane
4	$t\text{-}C_4H_9$	C_2H_5	0·126	$1{\cdot}67_0 \pm 0{\cdot}63_0$	$1{\cdot}4_8 \pm 2{\cdot}0_3$	*n*-octane
5	$i\text{-}C_4H_9$	C_2H_5	0·901	$0{\cdot}65_5 \pm 0{\cdot}02_9$	$1{\cdot}9_9 \pm 0{\cdot}0_9$	*n*-nonane
6	$n\text{-}C_5H_{11}$	C_2H_5	0·880	$0{\cdot}91_9 \pm 0{\cdot}05_7$	$2{\cdot}8_3 \pm 0{\cdot}1_8$	*n*-nonane
7	$CH_2{=}CH—$	C_2H_5	0·450	$0{\cdot}92_5 \pm 0{\cdot}05_9$	$1{\cdot}4_9 \pm 0{\cdot}1_9$	*n*-heptane
8	C_6H_5	C_2H_5	0·728	$0{\cdot}38_1 \pm 0{\cdot}07_9$	$0{\cdot}6_5 \pm 0{\cdot}3_1$	*n*-nonane
9	Cl	C_2H_5	4·522	$-0{\cdot}66_2 \pm 0{\cdot}13_7$	$0{\cdot}7_8 \pm 0{\cdot}4_4$	*n*-octane
10	C_2H_5O	C_2H_5	ca. 4	—	—	*n*-octane
11	CH_3	CH_3	0·968	$0{\cdot}91_3 \pm 0{\cdot}05_7$	$1{\cdot}4_8 \pm 0{\cdot}1_9$	*i*-pentane
12	CH_3	$i\text{-}C_4H_9$	1·431	$0{\cdot}43_1 \pm 0{\cdot}05_5$	$2{\cdot}1_6 \pm 0{\cdot}1_8$	*n*-octane
13	CH_3	$i\text{-}C_3H_7$	2·721	$-0{\cdot}56_8 \pm 0{\cdot}04_7$	$0{\cdot}0_9 \pm 0{\cdot}1_2$	*n*-heptane
14	CH_3	$t\text{-}C_4H_9$	3·378	$-0{\cdot}68_2 \pm 0{\cdot}13_5$	$0{\cdot}1_4 \pm 0{\cdot}4_3$	*n*-heptane

[a] Uncertainties are the probable errors.

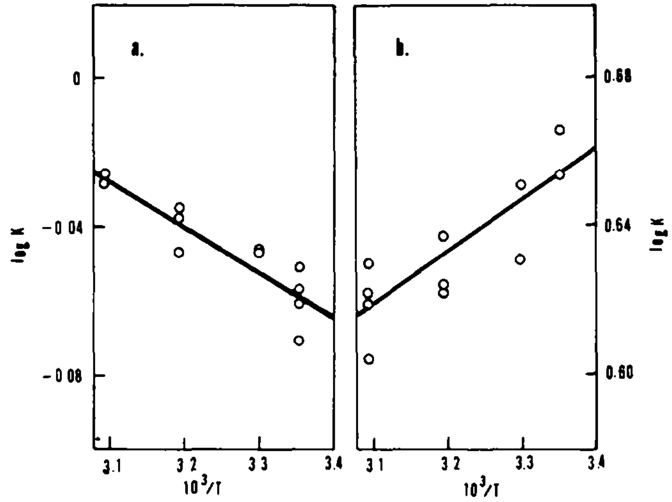


FIG. 2 Temperature dependence of isomerization equilibrium constants for (a) 1-butenyl and (b) β-chlorovinyl ethyl ethers.

vinyl ethyl ethers. The equilibrium data given in Table 2 indicate that both the enthalpy and entropy of alkenyl ethyl ethers (Nos. 1 to 6) increase on going from *trans* to *cis*. That is, *trans*-alkenyl ethyl ethers are *thermochemically* more stable than the *cis* ethers, and the entropy term (i.e., $-T\Delta S^\circ$) tends to favour the stability of the latter. The combined effect of the enthalpy and entropy on the relative abundance of the two isomers is a function of temperature. At 25°, the *trans* isomers of alkenyl ethyl ethers were also *thermodynamically* more stable than the *cis* isomers (i.e., $K < 1$), except where $R^1 = CH_3$ (No. 1).

The ΔH° for alkenyl ethyl ethers increases with the increasing number of the C atoms constituting the β-alkyl groups (R^1). A closer inspection of the ΔH° values seems to indicate that the thermochemical stability of the *trans* isomer relative to the *cis* isomer is also a function of the class of the alkyl substituents, increasing in the order: primary < secondary < tertiary. The physical significance of this trend is not clear.

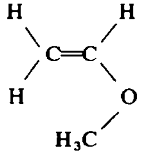
1,3-Butadienyl and styryl ethyl ethers (Nos. 7 and 8) are more stable in the *trans* form. In the case of styryl ether, the steric repulsion of the ethereal oxygen against the ortho hydrogen will prevent the *cis* isomer from taking the planar conformation and, thus, destabilize this isomer.

In the cases of β-chlorovinyl and β-ethoxyvinyl ethyl ethers (Nos. 9 and 10), the *cis* isomers were found to be the more stable, in contrast to the ethers carrying a nonpolar group on their β-carbon. 1,2-Dichloroethylene, which is iso-electronic with both β-chloro- and β-ethoxyvinyl ethers, is reported to be more stable in the *cis* form.[12] Some favourable interaction between the polar groups located at the positions *cis* to each other should be operative for these olefins. This interaction may possibly be due to the electronic structure and/or the attractive London dispersion force.[9]

Effects of the alkoxyl groups. The effects of the α-alkoxyl groups (R^2) on the relative *cis-trans* stability of unsaturated ethers were investigated for propenyl ethers. It is clear from Table 2 that the ΔH° values for propenyl alkyl ethers decrease in the order;

$R^2 = CH_3$ (No. 11) > $i\text{-}C_4H_9$ (No. 12) $\simeq$ C_2H_5 (No. 1) > $i\text{-}C_3H_7$ (No. 13) > $t\text{-}C_4H_9$ (No. 14). The bulkier alkoxyl group such as $i\text{-}C_3H_7O$ and $t\text{-}C_4H_9O$ showed an unexpected effect of stabilizing the *cis* ethers relative to the *trans* compounds. That is, propenyl ethers of methyl (No. 11) and other primary alcohols (Nos. 1 and 12) are thermochemically more stable in the *trans* form, while those of the secondary (No. 13) and tertiary alcohols (No. 14) are more stable in the *cis* form.

These results seem to be related with the conformation of the ethers (rotation about the sp^2 C—O bond). Several investigators claim that an unusual feature of the IR and Raman spectra of alkyl vinyl ethers may be taken as evidence for the presence of rotational isomers.[13] Cahill *et al.*[14] have recently demonstrated that methyl vinyl ether is of a planar *s-cis* structure (I). It was also ascertained that *s-cis*-methyl vinyl ether is more stable than the second-stable rotational isomer by 1·15 ± 0·25 kcal/mole in the vapour phase and by 0·66 ± 0·20 kcal/mole in 1,1,2-trichloroethane.[13]



I

s-cis-Isomers such as structure I may naturally become less stable as the alkoxyl group of vinyl ethers becomes bulkier. In fact, the presence of two IR absorption peaks assigned to each of the wagging and the twisting modes of the vinyl group and the variation of the relative prevalence of these peaks with the change in bulkiness of the alkoxyl group seem to be due to rotational isomerism.[15] Thus, methyl vinyl ether is predominantly of the *s-cis* form, whereas t-alkyl vinyl ethers are of non-*s-cis* form, the primary and secondary alkyl vinyl ethers lying in-between the above two cases.

These conformational effects must contribute to the stability of propenyl alkyl ethers. *cis*-Propenyl alkyl ethers cannot take the *s-cis* form because of steric repulsion between the methyl and alkyl groups *cis* to each other. On the other hand, *trans*-propenyl ethers are in the same situation as vinyl ethers so far as the rotational isomerism about the sp^2 C—O bond is concerned. Thus, in the case of propenyl methyl ether (No. 11), the *trans* isomer could take the stable *s-cis* form but the *cis* isomer could not exist in this form. Since an energy gain of the *trans* ether due to the rotational isomerism might be about 1kcal/mole, the stability of *trans*-propenyl methyl ether relative to the *cis* isomer may be ascribed mainly to the rotational isomerism.

In the same manner, both *cis*- and *trans*-propenyl t-butyl ethers (No. 14) are not of the *s-cis* form. Therefore, the stability of the former relative to the latter must primarily be due to the geometrical structure. The stability of other propenyl ethers will be a result of both geometrical and rotational isomerisms.

As a whole, the geometrical isomerism of propenyl alkyl ethers seems to energetically favour the *cis* form rather than the *trans* form, apart from rotational isomerism. It may be worth noting here that 1-halopropenes, which are isoelectronic with propenyl alkyl ethers, are considered to be more stable in the *cis* form.[8] The reason for the stability of *cis* isomers of these olefins is ambiguous.

Entropy change. Among the ethers investigated, propenyl ethers of secondary and tertiary alcohols (Nos. 13 and 14) show practically no change in entropy on isomerization. On the other hand, the entropy of β-substituted vinyl ethers of methyl and primary alcohols increases on going from *trans* to *cis*. That is, the entropy term (i.e., $-T\Delta S^\circ$) favours the stability of the *cis* isomer, independently of the thermochemical stability. These effects of entropy seem to be due mainly to the rotation about the sp^2 C—O bond. In the cases of secondary and tertiary ethers, the conformation of both geometrical isomers will essentially be the same, and as a result the entropy difference is small. However, the *s-cis* form of *trans* ethers of primary and methyl alcohols is considerably stable, and hence the entropy contribution to the stability of the *trans* isomers is smaller than that of the *cis* isomers, which cannot take such a stable conformational form.

EXPERIMENTAL

Materials. α,β-Unsaturated ethers were prepared by the methods described.[1-4] Mercuric acetate was the best commercial grade and was used without purification. Alkanes were purchased and distilled.

Procedure. Isomerization was carried out in bulk. The reaction mixture, consisting of mercuric acetate (ca. 0·1 g), an unsaturated ether (1 ml) of appropriate isomeric composition, and an alkane (0·5 ml) as internal standard for gas-chromatography, was kept at constant temp by a thermostat. At specified intervals, a small portion of the mixture (10 μl) was immediately subjected to gas-chromatography. During the determination, no sign of isomerization was observed. A Shimadzu gas chromatograph model GC-2C was operated with H_2 as carrier gas. A column packed with polyethylene glycol or Apiezon Grease L was used. Internal standards were selected so as to suit the determination of *cis* and *trans* isomers of each ether (see Table 2).

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