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(1) Although this statement may be an oversimplification of the conclusions of ref 2, it reflects the commonly expressed interpretation thereof. (See, for example, ref 3.)

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(9) It is surprising that thermally and photochemically generated carbene **1** produce identical isolatable product mixtures. However, a thermodynamic equilibration process is unlikely in the absence of Lewis acids (*e.g.*, Ag^+), as described by Roth and Katz.[6] Furthermore, more highly strained **3** survives more rigorous conditions in its preparation[3] than those described herein.

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Structure and Reactivity of α,β-Unsaturated Ethers. XV.[1] The Acid-Catalyzed Hydrolysis of Alkyl Propenyl Ethers. The Relative Cis/Trans Reactivity

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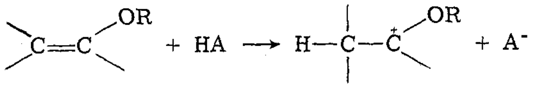
The acid-catalyzed hydrolysis of enol (α,β-unsaturated) ethers has widely been studied in recent years in the interest in its reaction mechanism.[2] It has been proved that the proton transfer to the unsaturated carbon is rate determining. This may be considered as a typical electrophilic addition reaction of the compounds of this class.



$$\gt C=C\lt^{OR} + HA \longrightarrow H-\overset{|}{\underset{|}{C}}-\overset{+}{C}\lt^{OR} + A^- \qquad (1)$$

We already carried out kinetic studies on the hydrolysis and the cationic polymerization of a variety of α,β-unsaturated ethers from the viewpoint of the structure–reactivity relationship. It was found that the cis isomers of alkenyl alkyl ethers are generally more reactive than the corresponding trans isomers.[3-6] The greater reactivity of the former isomers was at first considered to be due to its lower stability in the ground state.[3,4] Similar discussion has been made to interpret the relative reactivity of cis and trans alkenes in terms of the strain relief on reaction.[7,8]

Later on, however, we have found that the cis isomers of β-chloro- and β-alkoxyvinyl ethers, which are more stable than the trans counterparts,[10] are also more reactive.[5,6] Explanation of these specific cases was made in terms of the polar nature of the reacting molecule; more polar cis isomers should more readily be attacked by an electrophile.[5,6] One example of this trend appearing in the earlier literature is the chlorination of a polar olefin, 1,2-dichloroethylene, in which the stable cis isomer[11] is more reactive.[12]

Nevertheless, we still feel it necessary to confirm the generality of the greater reactivity of cis olefins toward electrophiles. The most desirable for this purpose is to obtain reactivity data for a series of olefins structurally similar to each other but thermochemically different in terms of their geometrical stability. As such a class of olefins, we have chosen in the present study alkyl propenyl ethers; methyl and primary alkyl ethers are more stable in their trans form than in the cis form, while the reverse is the case for secondary and tertiary alkyl ethers.[10] The acid-catalyzed hydrolysis was studied as a typical reaction of these ethers. All the cis isomers were found to be more reactive than their trans counterparts, irrespective of the ground-state stability.

Results

The acid-catalyzed hydrolysis of unsaturated ethers was carried out in acidic 80% aqueous dioxane ([HCl] = 0.01–0.02 *M*). The reaction was followed by the gas chromatographic determination of ether concentrations.[3] Although ether was subjected to the kinetic measurements as an isomeric mixture, each geometric isomer showed excellent first-order decay separately, indicating the absence of concurrent geometrical isomerization of reactant isomers.[3] The reaction was first order in acid and an ether.

$$\text{rate} = k_2[\text{HCl}][\text{ether}] \qquad (2)$$

The rate measurements for methyl propenyl sulfide (**8**) was undertaken in the same way in 80% aqueous tetrahydrofuran. The kinetic features observed were much the same as those found for ethers.

Rate constants so obtained are summarized in Table I, together with some earlier results. The activation parameters, ΔH^* and ΔS^*, were calculated in the usual way (by plotting $\log k_2/T$ against $1/T$) and included in Table I. The final two columns of Table I give the thermodynamic data, $\Delta H°$ and $\Delta S°$, for the cis–trans isomerization equilibria.[10] Negative values of ΔH^0 indicate greater thermochemical stability of the cis isomer in the liquid phase.

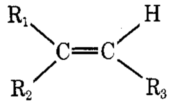
The data given in Table I show that the cis isomers are more reactive than the trans isomers for all the ethers studied here. The activation enthalpies, ΔH^*, of the former isomers are smaller than those for the latter, irrespective of their $\Delta H°$ values for the isomerization equilibria.

Discussion

Substituent Effects on the Reactivity. The reactivity of alkyl propenyl ethers increases in the order $CH_3 < C_2H_5 < i\text{-}C_3H_7 < t\text{-}C_4H_9$ for both the cis and trans isomers. The same order of the reactivity regarding the α-alkoxy group was previously observed with alkyl vinyl ethers[13,14] and alkyl ethynyl ethers.[15] This reactivity order of alkyl vinyl ethers is opposite to that expected from the electron density on the β-carbon atom of the vinyl group, which is deduced from the nmr data.[16-18] Undoubtedly, the reactivity should be accounted for from the stability of the transition state. The transition state of the reaction of the present concern resembles an intermediate carbonium ion,[3] which would be stabilized by the inductive electron donation by an alkyl group.

The reactivity of methyl propenyl sulfide (**8**) is about one-thousandth that of methyl propenyl ether (**1**), though the reaction medium is somewhat different. The same order of reactivity difference between S and O analogs was

Table I
Kinetic Data for the Acid-Catalyzed Hydrolysis[a] of α,β-Unsaturated Ethers



Compd	R_1	R_2	R_3	$10^4 k_2$,[b] $M^{-1}\text{sec}^{-1}$ 15°	25°	35°	45°	ΔH^*,[c] kcal/mol	ΔS^*,[d] eu	$\Delta H°$,[e] kcal/mol	$\Delta S°$,[e] eu
1c	H	CH_3	CH_3O	32.3	106	358		20.8	1.8	0.91	1.5
1t	CH_3	H	CH_3O	8.10	27.9	122		23.5	8.3		
2c[f]	H	CH_3	C_2H_5O	84.0	293	909		20.4	2.9	0.37	1.9
2t[f]	CH_3	H	C_2H_5O	22.6	90.3	299		22.2	6.5		
3c	H	CH_3	$i\text{-}C_3H_7O$	171	576	1720		19.9	2.4	−0.57	0.1
3t	CH_3	H	$i\text{-}C_3H_7O$	60.0	195	605		20.0	1.1		
4c	H	CH_3	$t\text{-}C_4H_9O$	303	870	2210		17.1	−5.8	−0.68	0.1
4t	CH_3	H	$t\text{-}C_4H_9O$	144	399	1080		17.3	−7.2		
5c[g]	H	C_2H_5O	C_2H_5O		3.23	11.1	36.0	20.7	−5.4	$[5c]_e/[5t]_e \sim 4$	
5t[g]	C_2H_5O	H	C_2H_5O		0.82	2.87	9.82	22.8	−0.9		
6c	H	Cl	C_2H_5O		0.68	2.37	7.03	21.6	−5.2	−0.66	0.8
6t	Cl	H	C_2H_5O		0.22	0.89	3.59	25.5	5.8		
7c	H	Br	C_2H_5O		2.38	7.72	21.5	20.1	−7.9		
7t	Br	H	C_2H_5O		0.72	2.85	8.78	23.0	−0.3		
8c[h,i]	H	CH_3	CH_3S			0.361	1.82	25.7	4.6		
8t[h,j]	CH_3	H	CH_3S			0.249	1.50	28.4	12.7		

[a] In 80% aqueous dioxane. [b] Given as an average of at least two measurements. [c] Accurate to within ±0.2 kcal/mol. [d] Accurate to within ±0.5 eu. [e] Values for the equilibrium trans ⇌ cis. Data were taken from ref 10. [f] Kinetic data were taken from ref 3. [g] Kinetic data were taken from ref 6. [h] Hydrolysis was carried out in 80% aqueous THF. [i] $k_2 = 4.92 \times 10^{-4} M^{-1} \text{sec}^{-1}$ at 55°. [j] $k_2 = 4.45 \times 10^{-4} M^{-1} \text{sec}^{-1}$ at 55°.

previously observed for the acetylenic ethers.[15,19] These differences will be ascribable to the diminished electron-donating conjugation ability of the thio group with 3p orbitals in the reactant and/or intermediate carbonium ion as compared with that of alkoxy group.

β-Alkoxy- and β-halogenovinyl ethers are less reactive than the propenyl ethers by a factor of 10^{-3} to 10^{-4}. In this case, the conjugative stability of the ground state due to the lone-pair electrons of a β substituent might be responsible for the reduced reactivity.

Relative Cis/Trans Reactivity. The results given in Table I show that all the cis isomers are more reactive than the corresponding trans isomers. The activation enthalpies, ΔH^*, are correspondingly greater for the trans isomers, irrespective of the relative cis/trans ground-state stability. That is, the greater reactivity of the cis isomers is enthalpy controlled in the ordinary temperature region. Similar tendency of the cis/trans reactivity was previously observed in the cationic polymerization of unsaturated ethers.[4-6,20-22]

It might safely be concluded that the greater reactivity of the cis isomers is quite general in electrophilic additions to olefins. Various kinetic results available in the literature[23] conform to this generalization. Some available examples which clearly do not fall in this generalization should be explained by certain other factors. For instance, hydrochlorination of *cis*-1-phenylpropene was concluded to be affected by the adverse steric effects arising from its nonplanar structure; if it were planar in structure, it would be (electronically) more reactive than the trans isomer.[24]

On the whole, the relative cis/trans reactivities in electrophilic addition reactions of olefins cannot be accounted for only by the ground-state properties of olefins. Some intrinsic electronic factor that operates on going from the ground to the transition state may control these reactivities. A theoretical molecular orbital calculation indeed demonstrates this point, which will be fully described elsewhere.[25] In brief, the Coulombic term of the interaction energy between an electrophile and an olefin at the transition state generally favors the cis structure of olefinic moiety. This Coulombic interaction must be a major factor contributing to the greater reactivity of the cis olefins in electrophilic additions.

On the contrary, in homolytic addition reactions where the Coulombic contribution is small, the charge-transfer interaction predominates and the trans isomers whose ionization potential is smaller are more reactive.[25] The charge-transfer interaction could well predominate even in electrophilic additions for exceptional cases, such as an olefin of low ionization potential plus an electrophile of low electron affinity. Such a case was actually encountered in sulfenyl chloride addition to 1-arylpropenes, in which the trans isomer was electronically more reactive.[26]

In conclusion, the cis olefins are generally more reactive in electrophilic addition reactions than the corresponding trans isomers, because of the favorable Coulombic interaction energy in the transition state.

Experimental Section

Materials. *cis*- and *trans*-Propenyl isopropyl ether (**3c** and **3t**)[21] and *cis*- and *trans*-β-chlorovinyl ethyl ether (**6c** and **6t**)[6] were obtained as described previously, *cis*- and *trans*-propenyl methyl ether (**1c** and **1t**) were prepared in the same way as before;[3] cis/trans ~1.5, bp 45–46° (lit.[27] **1c**, 45.0° and **1t**, 48.5°). *cis*- and *trans*-propenyl *tert*-butyl ether (**4c** and **4t**) were prepared by the alcohol exchange from propenyl ethyl ether (a mixture of **2c** and **2t**).[28] The yield of a mixture of **4c** and **4t** (~4:1) was about 20%, bp 101–102° (lit.[29] **4c**, 101°).

cis- and *trans*-β-bromovinyl ethyl ether (**7c** and **7t**) were prepared from paraldehyde and bromine by the method of Jacobs, *et al.*[30] The isomeric composition (cis/trans) was ~3.5, bp 44–52° (20 mm) [lit.[30] 41–44° (19 mm)].

cis- and *trans*-propenyl methyl sulfide (**8c** and **8t**) were obtained by the rearrangement of allyl methyl sulfide,[31] bp 102–103° (lit.[32] 102°).

Geometrical structure of the ethers was assigned by pmr spectra.

Kinetic Measurements. The reaction of unsaturated ethers was carried out in 80% aqueous dioxane and the rates were measured gas chromatographically by the method described previously.[3] The hydrolysis of **8c** and **8t** was carried out in 80% aqueous tetrahydrofuran. In most cases a mixture of cis and trans isomers was subjected to hydrolysis but analyzed separately.

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Registry No.—**1c**, 4188-68-5; **1t**, 4188-69-6; **2c**, 4696-25-7; **2t**, 4696-26-8; **3c**, 4188-64-1; **3t**, 4188-65-2; **4c**, 4188-71-0; **4t**, 4188-72-1; **5c**, 4884-01-9; **5t**, 1528-20-7; **6c**, 23679-21-2; **6t**, 23679-22-3; **7c**, 23521-49-5; **7t**, 16339-88-1; **8c**, 52195-40-1; **8t**, 42848-06-6.

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Quasi-Favorskii Rearrangement. Synthesis of 1-Phenylcycloalkanecarboxylic Acids[1]

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The skeletal rearrangement of α-halo ketones having an α' hydrogen atom on treatment with certain nucleophiles such as hydroxides, alkoxides, or amines to give carboxylic acid salts, esters, or amides, respectively (Favorskii reaction) is well known and has been extensively investigated.[3,4] α-Halo ketones which do not have an α' hydrogen atom[5,6] and certain α-halo ketones with α' hydrogen attached to a bridgehead carbon atom[7,8] also undergo similar rearrangement, although by a different ("semibenzilic") mechanism, and may be called the "quasi-Favorskii reaction." Stevens and Farkas[5] and later Kirmann and Joschek[9] suggested that heterogeneous conditions are required for this rearrangement, as homogeneous conditions resulted in the direct replacement of the α halogen by the nucleophile. We now report a quasi-Favorskii rearrangement of α-halo ketones by the lithium salt of aromatic primary amines under homogeneous conditions. The resulting amides were hydrolyzed to the corresponding carboxylic acids, some of which are very difficultly obtained by other methods.

The reaction of α-bromo ketones with lithium anilide was investigated as a general method for the synthesis of α-anilino ketones. Although treatment of 1-benzoyl-1-bromocyclopentane[10] (**1a**) with lithium anilide in ether provided 87% of the amino ketone **2**, 1-benzoyl-1-bromocyclohexane[5a] (**4a**) under the same conditions gave only 30% of the corresponding amino ketone, **6**. The major product (55%) was 1-phenylcyclohexanecarboxanilide[11] (**5**), formed by a quasi-Favorskii rearrangement. When the α-chloro ketone,[5a] **4b**, was used in the place of **4a**, the proportion of the anilide[6] formed was increased to 62% at the expense of the anilino ketone, **6** (21%). This result is in agreement with an earlier observation[5a] in the rearrangement studies under heterogeneous conditions. Amino ketones **2** and **6** were further characterized by their reduction with sodium borohydride to the amino alcohols **3** and **7**, respectively.