The Role of Ion-Molecule Pairs in Solvolysis Reactions. **Nucleophilic Addition of Water to a Tertiary Allylic Carbocation**

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The acid-catalyzed solvolysis of 2-methoxy-2-phenyl-3-butene (1-OMe) in 9.09 vol % acetonitrile in water provides 2-hydroxy-2-phenyl-3-butene (1-OH) as the predominant product under kinetic control along with the rearranged alcohol 1-hydroxy-3-phenyl-2-butene (2-OH) and a small amount of the rearranged ether 2-OMe. The more stable isomer 2-OH is the predominant product after long reaction time, $K_{eq} = [2-OH]_{eq}/[1-OH]_{eq} = 16$. The ether 2-OMe reacts to give 2-OH and a trace of 1-OH. Solvolysis of 1-OMe in ¹⁸O-labeled water/acetonitrile shows complete incorporation of ¹⁸O in the product **1-OH**, confirming that the reaction involves cleavage of the carbon–oxygen bond to the allylic carbon. A completely solvent-equilibrated allylic carbocation is not formed since the solvolysis of the corresponding chloride 1-chloro-3-phenyl-2-butene (2-Cl) yields a larger fraction of 1-OH. This may be attributed to a shielding effect from the chloride leaving group. Quantum chemical calculations of the geometry and charge distribution show that the cation should rather be described as a vinyl-substituted benzyl cation than as an allyl cation, which is in accord with its higher reactivity at the tertiary carbon.

Introduction

Stepwise solvolytic reactions of substrates with neutral leaving groups produce carbocation molecule pairs (iondipole pairs) by cleavage of the bond between the carbon and the leaving group (Scheme 1).1-11 The diffusional separation (k_{-d}) to give a solvent-equilibrated carbocation is expected to be fast ($k_{-d} \sim 2 \times 10^{10} \text{ s}^{-1}$) in aqueous solution which means that a bimolecular reaction with a dilute reactant should not be able to compete with the separation. Accordingly, a substantial amount of reaction of the ion-molecule pair R⁺X should require either an intramolecular reaction, e.g., a rearrangement reaction to give R'X⁺ (Scheme 1) or an elimination reaction in which the leaving group acts as the hydron-abstracting base, or a bimolecular reaction with a species which is close to R⁺X when it is born.

We have previously reported studies on reactions which give products directly through the ion-molecule pair.^{2,5-9} These studies suggested that the nature of the carbocation and the basicity of the leaving group are of crucial importance for the product composition. The present report concerns the mechanisms of nucleophilic addition

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to an allylic carbocation and to its complexes with methanol and other leaving groups.

The study is closely related to the question about the lifetime of simple tertiary carbocations in water and highly aqueous solvents. Recently, Toteva and Richard discussed the lifetime of the *tert*-butyl carbocation.¹² Reactivity data obtained from studies of less reactive carbocations were extrapolated by employing the extended Hammett relationship to give an estimated rate constant for reaction of the tert-butyl carbocation with solvent (50 vol % 1,1,1-trifluoroethanol in water) of $k_{\rm s} \sim$ $1.6 \times 10^{12} \text{ s}^{-1}$. This value suggests that the carbocation is not diffusionally equilibrated but reacts at the ion-pair stage within the pool of solvent molecules that are present when the bond to the leaving group is broken.

The results of the present study suggest that also a more stable benzallylic cation reacts to some extent with a solvent water molecule of the solvation shell that is present at the time of ionization, before separation takes place.

Results

Reactions of Ethers and Alcohols. The acidcatalyzed solvolysis of 2-methoxy-2-phenyl-3-butene (1-**OMe**) in 50 vol % acetonitrile in water at 25 °C yields

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Figure 1. The time dependence of the product composition of the acid-catalyzed solvolysis of **1-OMe** (Scheme 2) in 50 vol % acetonitrile in water at 25 °C: pH 1.90 and $[NaClO_4] = 0.10$ M. The points are the experimental data, and the curves are computer simulated using eqs 5–7. The formation of the small amount of **2-OMe** is not included.



the alcohols 2-hydroxy-2-phenyl-3-butene (1-OH) and 1-hydroxy-3-phenyl-2-butene (2-OH) and a trace of 1-methoxy-3-phenyl-2-butene (2-OMe) (Scheme 2). The change in product composition as a function of time is shown in Figure 1. The alcohol product 1-OH is less stable than its allylic isomer 2-OH and after a long reaction time most of **1-OH** has been converted to **2-OH**. The equilibrium constant was measured in a separate experiment by studying the acid-catalyzed formation of 2-OH from **1-OH**, $K_{eq} = [2-OH]_{eq}/[1-OH]_{eq} = 16 \pm 2$. The solvolysis of **1-OMe** in a less aqueous solvent mixture (91.09 vol % acetonitrile in water) gives somewhat more of the rearrangement product 2-OMe, but has only a small effect on the alcohol product ratio. A more aqueous solvent (9.09 vol % acetonitrile in water) increases the alcohol product ratio [1-OH]/[2-OH].

The kinetics of the reaction of **1-OMe** as well as of its allylic isomer **2-OMe** and the corresponding alcohols **1-OH** and **2-OH** were studied by a high-performance liquid chromatography sampling procedure. The reaction of **1-OH** was also followed by UV spectrophotometry. The rate constants and reaction conditions are recorded in Table 1. The observed rate constant for the reaction of **1-OMe** was divided into the separate phenomenological rate constants by employing a computer simulation technique (Figure 1; see Experimental Section for details).

Table 1. Rate Constants for the Acid-Catalyzed Reactions of 1-OMe, 2-OMe, and 1-OH in Aqueous Acetonitrile at 25 °C

substrate	vol % MeCN	$10^6 k_{\rm obs}$, ^a s ⁻¹	$k_{ m H}$, ${ m M}^{-1}{ m s}^{-1}$	$\frac{10^6k_{\rm AB}}{\rm s}^{-1}$	$10^{6}k_{\rm AC},\ {\rm s}^{-1}$	$10^{6}k_{AD}, s^{-1}$
1-OMe	9.09 50 91.09	103.0^{b} 54.8 ^c 72.1 ^d	$\begin{array}{c} 88 \times 10^{-3} \\ 4.3 \times 10^{-3} \end{array}$	82.0 39.0 52.2	21.0 15.5 18.8	0.16 0.3 1.1
2-OMe 1-OH	50 50 50	$ \begin{array}{r} 1.4^{e} \\ 4.5^{c,f} \\ (568)^{g} \end{array} $	$\begin{array}{c} 4.6 \times 10^{-6} \\ 357 \times 10^{-6} \\ (931 \times 10^{-6}) \end{array}$	02.2	10.0	1.1

^{*a*} Estimated maximum errors: \pm 5%. ^{*b*} pH 2.93 and [NaClO₄] = 0.10 M before mixing with acetonitrile. ^{*c*} pH 1.90 and [NaClO₄] = 0.10 M before mixing with MeCN. ^{*d*} [HClO₄] = 51 mM before mixing with MeCN. ^{*e*} [HClO₄] = 0.304 M and [NaClO₄] = 0.40 M before mixing with MeCN. ^{*f*} Equilibrium constant [**2-OH**]_{eq}/[**1-OH**]_{eq} = 16 ± 2. ^{*g*} [HClO₄] = 0.61 M and [NaClO₄] = 0.40 M before mixing with MeCN; rate constant measured by UV spectrophotometry.

Table 2. Rate Constants for the Solvolysis Reactions of 1-PNB, 2-PNB, and 2-Cl in 50 Vol % Acetonitrile in Water at 25 $^\circ\mathrm{C}$

substrate	addition	$10^{6}k_{\rm obs}$, ^a s-1	${10^6 k_{ m r}}, {{ m s}^{-1}}$	[1-OH]/ [2-OH]	[1-SCN]/[2-SCN] or [1-OMe]/[2-OMe]
1-PNB	none	179	33	2.8 ± 0.1	
1-PNB	SCN ^{-b}	370	12	2.8 ± 0.2	0.11 ± 0.05
1-PNB	MeOH ^c			2.5 ± 0.1	6.0 ± 0.4
2-PNB	none	$\sim 0.03^d$		$0.9^d \pm 0.1$	
2-Cl	none	fast		4.1 ± 0.2	
2-Cl	$MeOH^{c}$	fast		2.1 ± 0.1	1.8 ± 0.1

^{*a*} Estimated maximum errors: $\pm 7\%$. ^{*b*} [NaSCN] = 0.25 M; pH = 6.8. Reaction with 0.25 M NaClO₄ gave $k_{obs} = 357 \times 10^{-6} \text{ s}^{-1}$, pH = 6.8. ^{*c*} [MeOH] = 0.75 M. ^{*d*} 5% reaction after 20 days. ^{*e*} [1-OH]/[2-OH] = 1.0 at 60 °C.

It was not possible to carry out trapping experiments with azide ion owing to the low pH required for the reactions. Addition of chloride or bromide ion (0.20 M) did not give rise to any detectable substitution product.

Solvolysis experiments in oxygen-labeled water were performed in order to establish which of the two carbon– oxygen bonds in the substrate is broken during the reaction. Thus, the acid-catalyzed solvolysis of **1-OMe** in a mixture of ¹⁸O-labeled water with 50 vol % acetonitrile was followed by a GC/MS sampling procedure. The analysis showed complete incorporation of the labeled oxygen into the product **1-OH**, as well as in the product **2-OH**, confirming that it is the tertiary carbon–oxygen bond that is broken (see Experimental Section for details).

Reactions of Esters and Chloride. The solvolysis of 2-(4-nitrobenzoyl)-2-phenyl-3-butene (**1-PNB**) in 50 vol % acetonitrile in water at 25 °C provides the alcohols **1-OH** and **2-OH** and some of the rearranged substrate 1-(4-nitrobenzoyl)-3-phenyl-2-butene (**2-PNB**). The rearrangement of the ester **1-PNB** is about 4 times slower than the formation of the alcohols (Table 2). This rearranged ester reacts much more slowly, and no trace of **1-PNB** was observed along with the alcohols after 20 days of reaction (~5% reaction). The very fast solvolysis of 1-chloro-3-phenyl-2-butene (**2-Cl**) exclusively provides the alcohols. The results of these reactions are shown in Table 2.

Azide-trapping experiments with the ester **1-PNB** did not work owing to a complex reaction product mixture. The solvolysis of **1-PNB** in the presence of thiocyanate ion (0.25 M) does not increase reaction rate compared with perchlorate ion but gives two major products, **1-SCN**



Figure 2. CC Bond distances (Å) and atomic charges (electron) for 1a calculated at B3LYP/6-31G(d) (normal print) and PCM B3LYP/6-31G(d) (italics) levels.



and 2-SCN, along with the alcohols. A trace of 2-NCS is also formed. These substitution products are stable under the reaction conditions. The nucleophilic selectivity between thiocyanate ion and water was derived from the measured product composition as $k_{\text{SCN}}/k_{\text{HOH}} = 190$ (ratio of second-order rate constants, eq 1). Assuming a diffusion-controlled reaction of thiocyanate ion ($k_{\rm d} = 5 \times 10^9$ $M^{-1} s^{-1}$) with the carbocation yields $k_w = 7 \times 10^8 s^{-1}$ (eq 2).

 $k_{\rm SCN} / k_{\rm HOH} = ([thiocyanate products]/[alcohol])$ products])/([SCN⁻]/[HOH]) (1) $k_{\rm w} = ([\text{alcohol products}]/[\text{thiocyanate products}]) \times$

 $k_{\rm d} \times [\rm{SCN}^-]$ (2)

Calculations. The *s*-trans conformer (1a in Figure 2) of the cation is 1.0 kcal/mol more stable than the s-cis isomer at the B3LYP/6-31G(d) level of calculation. The optimal CC bond lengths and atomic charges at the C atoms, as calculated with natural population analysis, are given for 1a in Figure 2. The B3LYP geometry reveals a bond length difference between the C1-C2 and C2-C3 bonds by 0.084 Å, contrary to the allyl cation where these bond lengths are identical (1.385 Å). In addition, C3 is more positively charged and C1 is more negatively charged than the corresponding C atoms in the allyl cation (0.003 e). Geometry optimization of the cation, using the polarizable continuum model (PCM) of Tomasi and co-workers with the dielectric constant set as for water, did neither change geometry to any major extent nor charge distribution (Figure 2). The relative stabilities of the two conformers were changed slightly, but 1a is more stable by 1.4 kcal/mol. Support for the rather extensive stabilizing effect of the allyl cation by the phenyl group in 1 is obtained through the isodesmic reaction 1 shown in Scheme 3. The additional stabilization when going from the 1-methylallyl cation in the s-cis



conformation to the s-trans isomer 1a is 33.8 kcal/mol at B3LYP/6-31G(d) level. However, when going from cumyl cation to 1a (reaction 2, Scheme 3), only 11.3 kcal/mol are released.

Discussion

The ether **1-OMe** is relatively unreactive in acidic solution, it reacts about 10³ times slower than the structurally related 1-methoxy-1-methyl-1,4-dihydronaphthalene (3 in Scheme 4).¹³ This is presumably the result of extensive charge delocalization accompanying the ionization of the latter compound (vide infra). The carbocation is stabilized by enhanced resonance in the cyclic carbocation.¹⁴ A comparison with the structurally related cumyl methyl ether (4 in Scheme 4) shows that 1-OMe is 10² times more reactive.¹⁵

The reactivity of the carbocation has been measured by trapping the intermediate(s) formed from the ester 1-PNB with thiocyanate ion (see Results). A rate constant for reaction of the carbocation of $k_{\rm w} = 7 \times 10^8 \, {\rm s}^{-1}$ was obtained. This could be compared with the reactivity of other structurally related carbocations. There are a few relevant reports in the literature. For example, the allylic carbocation $\mathbf{5}^+$ (Scheme 4)^{2,16} reacts with water in 75% aqueous acetonitrile with a rate constant of $k_w = 4$ \times 10 $^9\,s^{-1}$ which is similar to that of the cumyl cation $4^{+,\,15}$ The cation 6^+ in 20% aqueous acetone shows a lower reactivity, $k_w = 4 \times 10^8 \text{ s}^{-1}$.¹⁷ This should correspond to a value of about $1 \times 10^9 \, s^{-1}$ in 50 vol % acetonitrile. The tertiary benzallylic carbocation is expected to be more stable than these ions, but it should be less stable than the cation 7⁺ which reacts with water with a rate constant of $k_{\rm w}\sim 1\, imes\,10^7~{
m s}^{-1.18}$ All these estimated reactivities are based upon the assumption that the cations are diffusionally equilibrated. However, this is presumably not quite correct (vide infra).⁵

The pK_R for the pseudo acid-base equilibrium for cation hydration (eqs 1 and 2) is a measure of the thermodynamic stability of a carbocation \mathbf{R}^+ .

$$\mathbf{R}^{+} + \mathbf{H}_{2}\mathbf{O}\frac{\mathbf{k}_{w}}{\mathbf{k}_{H}}\mathbf{R}\mathbf{O}\mathbf{H} + \mathbf{H}^{+}$$
(3)

$$pK_{\rm R} = \log(k_{\rm H}/k_{\rm w}) \tag{4}$$

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The estimated reactivity of the solvent-equilibrated benzallylic carbocation with water of $k_{\rm w} = 7 \times 10^8 \ {\rm s}^{-1}$ (vide supra) and $k_{\rm H} = 357 \times 10^{-6} \ {\rm M}^{-1} {\rm s}^{-1}$ (Table 1) yields p $K_{\rm R} = -12.3$. This could be compared with the value for the cyclic benzallylic carbocation 7⁺ (Scheme 4), which has been estimated as p $K_{\rm R} \sim -7.8$.¹⁸

The ionization rate constant k_1 should be relatively insensitive to the solvent polarity in sharp contrast to the cleavage of a bond between carbon and a negatively charged leaving group. Also, the rearrangement of the two localized ion-molecule pairs (k_r , Scheme 5) is not expected to show a high sensitivity to the solvent polarity. This allylic rearrangement of the ion-molecule pairs involves breaking of the dipole interaction between the carbocation and the leaving group and formation of a new one between carbon 3 and the leaving group combined with adjustments of electron density and geometry of the allylic system. These processes are expected to be relatively fast with a maximum rate constant of about 1 imes10¹¹ s⁻¹.^{19,20} A rate constant of this magnitude has been proposed for the reorganization of thionobenzoate pairs in 50% aqueous trifluoroethanol.²¹

The primary allylic alcohol **2-OH** is more stable than its allylic tertiary isomer **1-OH**, $K_{eq} = [2-OH]_{eq}/[1-OH]_{eq}$ = 16. However, **1-OH** is the predominant product under kinetic control. It is formed 2.5 times faster than **2-OH** (Table 1). The ester **1-PNB** shows a similar rate-ratio but exhibits more allylic rearrangement than **1-OMe** (Table 2). Two plausible alternative explanations for the predominant formation of **1-OH** are the following. (i) Direct reaction of the *localized* ion-molecule pair **1**⁺O(H)Me with solvent water ($k_{w'}$, Scheme 5). (ii) Reaction through the solvent-equilibrated allylic carbocation; a smaller kinetic barrier for addition of water to the tertiary carbon than to the primary carbon.

The first alternative is supported by the fact that there is a significant *increase* in the product alcohol ratio **[1-OH]**/**[2-OH]** with increasing fraction of water in the solvent (from 2.5 to 3.9 for an increase in water content from 50 to 91%); an approximately constant ratio is expected for reaction through the solvent-equilibrated carbocation. A substantial amount of direct reaction of $1^+O(H)$ Me with water before dissociation (k_{-d}) requires that k_w' is comparable to k_{-d} , which should have a value of about $2 \times 10^{10} \text{ s}^{-1}$, and also comparable to k_r , which is expected to have a maximum value of about $1 \times 10^{11} \text{ s}^{-1}$ (Scheme 5, vide supra).

The rate constant for rotation of a water molecule into a reactive position in a solvation shell should be similar to that for the dielectric relaxation of water which occurs with a rate constant of $\sim 10^{11}~s^{-1.19,20}$ The rate-limiting step for addition of a solvent water molecule to a very unstable carbocation is expected to be this rotation of the water molecule into a reactive orientation. However, the absence of a significant bonding barrier for the addition of a water molecule to the cation of the benzallylic ion-molecule pair 1+O(H)Me may not seem reasonable. Let us look at the other alternative explanation to the predominant formation of 1-OH.

The second alternative that the alcohols are formed from a solvent-equilibrated allylic carbocation which has a smaller barrier for addition of the water to the tertiary than to the primary carbon is in accord with the large fraction of 1-OH formed from 2-Cl. This large fraction (80%, Table 2) is not expected to be caused by a $S_N 2'$ reaction owing to the steric hindrance at the benzylic carbon, but is reasonably the result of a stepwise carbocation mechanism. The larger fraction of 1-OH formed from 2-Cl than from 1-OMe is consistent with a shielding effect of the leaving group in the allylic ion pair.⁵ Thus, the carbocation is *not* a completely free solvent-equilibrated species but reacts to a significant extent with a solvent water molecule of the solvation shell that is present at the time of ionization. The very small amount of 1-OH formed from 2-OMe may seem to be inconsistent with a common carbocation intermediate. However, **2-OMe** is much less reactive, and any **1-OH** formed may quickly undergo further reaction to give the other, thermodynamically more stable alcohol product 2-OH. The product ratio of [1-OH]/[2-OH] = 2.5 corresponds to a difference in kinetic barrier of 0.5 kcal/mol. A similar product ratio was measured with 1-PNB (Table 2). However, the ratio measured with thiocyanate ion was much smaller, [1-SCN]/[2-SCN] = 0.1 (Table 2). This value probably reflects the thermodynamic stabilities of these products.

The rate constant for the collapse of the ion-molecule pair to give **2-OMe** should have a rate constant of about $1 \times 10^8 \text{ s}^{-1}$ based upon $k_{-d} = 2 \times 10^{10} \text{ s}^{-1}$ and the measured rate constants in 50% aqueous acetonitrile (Table 1).

Another alternative explanation for the large amount of **1-OH** formed might have been an $S_N 2$ reaction in which water attacks the methyl group of the hydronated substrate. However, this possibility is excluded since solvolysis experiment with ¹⁸O-labeled water showed complete incorporation of the labeled oxygen in **1-OH**.

Do quantum chemical calculations support the conclusion that the addition of water to the tertiary carbon has the lowest barrier? Our results indicate a much higher charge density at the tertiary carbon. The results reveal that the cation should rather be described as a vinyl-substituted α -methylbenzyl carbocation than as an allyl cation (Figure 2), consistent with the higher reactivity of the tertiary carbon. The charge distribution and geometry are very similar in gas phase and in water. The substitution of a methyl with a vinyl group in the cumyl carbocation $\mathbf{4}^+$ (Scheme 4) corresponds to a rate increase of the methyl ether of 2 orders of magnitude and to a 5-fold decrease in k_w .¹⁵

The result of the present work is closely related to an earlier study on acid-catalyzed solvolysis of allylic ethers in highly aqueous solution (Scheme 6) in which we reported that allylic rearrangement of the methyl ethers accompanies formation of the alcohols.² The isomerization

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of **5-OMe** is much more competitive with alcohol formation than the isomerization of **1-OMe**. It was suggested that two discrete ion-molecule pairs are involved, but, owing to fast equilibration of the allylic alcohols, it was not possible to detect any possible fast direct reaction of the localized ion-molecule pair with solvent water. A single common ion-molecule pair mechanism was concluded to be inconsistent with the data since the collapse ratio for formation of the two ethers derived from the kinetic data was found to be smaller than the one measured for the corresponding tertiary chloride **8-Cl** in aqueous acetonitrile with added methanol (Scheme 6). However, alternatively, the results may be rationalized by a shielding effect of the chloride ion as was discussed above.

Recently, we reported studies on acid-catalyzed solvolysis of 1-methoxy-1,4-dihydronaphthalene and 1-methoxy-1-methyl-1,4-dihydronaphthalene (3, Scheme 4) in highly aqueous solution.^{13,18} No formation of the corresponding 1-hydroxy derivatives was found in these studies. These observations were rationalized by postulating that the carbon-oxygen bond cleavage is accompanied by extensive delocalization of charge. This is in accord with the approximately 10^3 times greater reactivity of **3** compared with 1-OMe and with the large driving force of the reactions giving naphthalene and methylnaphthalene; the reaction heats for the corresponding alcohols were measured as -23.7 and -21.7 kcal/mol, respectively.^{13,18} The extensive charge delocalization which accompanies the ionization results in a large barrier for the back reaction (the formation of the reactant ether) as well as for the collapse to give the corresponding alcohol.

Experimental Section

General Procedures. NMR spectra were recorded at 25 °C with a Varian Unity 300 or 400 MHz spectrometer. Chemical shifts are indirectly referenced to TMS via the solvent signal (chloroform-d 7.26 and 77.0 ppm). The highperformance liquid chromatography analyses were carried out with a Hewlett-Packard 1090 liquid chromatograph equipped with a diode-array detector on an Inertsil 3 ODS-3 (3 \times 100 mm) reversed-phase column. The mobile phase was a solution of acetonitrile in water. The reactions were run at constant temperature controlled by a HETO 01 PT 623 thermostat bath. The kinetics using UV spectrophotometry were carried out with a Kontron Uvicon 930 spectrophotometer equipped with an automatic cell changer kept at constant temperature with water from the thermostat bath. The pH was measured using a Radiometer PHM82 pH meter with an Ingold micro glass electrode. The pH values given are those measured before mixing with the organic solvent. The mass spectrometric analyses were carried out on a GC/MS instrument of quadrupole iontrap type (Finnigan MAT GCQ equipped with autosampler AS-2000 and an OV-5, 30 m \times 0.25 mm GC column).

Materials. Merck silica gel 60 (240–400 mesh) was used for flash chromatography. Diethyl ether and tetrahydrofuran were distilled under nitrogen from sodium and benzophenone. Methanol and acetonitrile were of HPLC quality and HPLC UV gradient quality, respectively. All other chemicals used for the kinetic experiments were of reagent grade and used without further purification. The oxygen labeled water was delivered from Isotec Inc. (>95 at. % ¹⁸O).

2-Hydroxy-2-phenyl-3-butene (1-OH) was prepared by addition of vinylmagnesium bromide to acetophenone in tetrahydrofuran.²² Distillation of the product gave pure material.

1-Hydroxy-3-phenyl-2-butene (2-OH) was prepared by Reformatsky reaction of acetophenone with ethyl bromoacetate followed by reduction with lithium aluminum hydride.^{23,24}

2-Methoxy-2-phenyl-3-butene (1-OMe) was prepared from **1-OH** by methylation with methyl iodide in tetrahydro-furan and distilled. Purity was confirmed by NMR²⁵ and HPLC.

1-Methoxy-3-phenyl-2-butene (2-OMe).²⁵ A methanol solution (30 mL) of the alcohol **1-OH** (0.37 g) and perchloric acid (1.5 g, 75%) was kept at room temperature for 3 h. Extraction with diethyl ether, drying, and flash chromatography with pentane-diethyl ether on a silica column gave a product free from alcohols and **1-OMe**.

2-(4-Nitrobenzoyl)-2-phenyl-3-butene (**1-PNB**). Methyllithium (0.6 mL, 1.6 M in diethyl ether) was added to a solution of **1-OH** (0.122 g, 0.82 mmol) in dry tetrahydrofuran under nitrogen at 0 °C; the solution was stirred for further 30 min. A solution of 4-nitrobenzoyl chloride (0.178 g, 0.96 mmol) in tetrahydrofuran (5 mL) was then added. After 5 h of stirring, the reaction mixture was poured into water, extracted with ether, and dried over magnesium sulfate. Removal of solvent and recrystallization twice from pentane gave yellow crystals (yield 70 mg, 25%). The purity was confirmed by NMR and HPLC; ¹H NMR (CDCl₃): 2.056 (s, 3 H), 5.36 (d, 1 H, J = 10.8Hz), 5.403 (d, 1 H, J = 17.6), 6.40 (q, 1 H, J = 17.6 Hz, 10.8 Hz).

1-(4-Nitrobenzoyl)-3-phenyl-2-butene (**2-PNB**). A solution of butyllithium (2.2 mL, 2.5 M in hexane) was added dropwise to a solution of **2-OH** (0.81 g, 5.5 mmol) in 10 mL of dry diethyl ether at 0 °C. After 10 min of further stirring, a solution of 4-nitrobenzoyl chloride (1.02 g, 5.5 mmol) in 10 mL of dry diethyl ether was added. The reaction mixture was worked up after 16 h. Purification by flash chromatography on a silica column gave pure material, yield 0.58 g, (36%); ¹H NMR (CDCl₃) 2.20 (s, 3 H), 5.09 (d, 2 H, 7.2 Hz), 6.03 (ddd, 1 H, J = 1.6 Hz, 7.2 Hz), 7.27–7.45 (m, 5 H), 8.22–8.31 (m, 4 H).

1-Chloro-3-phenyl-2-butene (**2-Cl**) was prepared from **2-OH** and thionyl chloride followed by distillation.²³

Kinetics and Product Studies. The reaction solutions were prepared by mixing acetonitrile with aqueous perchloric acid solutions at room temperature, ca. 22 °C. The reactions were initiated by addition of a few microliters of the substrate dissolved in acetonitrile to a 2-mL HPLC vial containing 1.2 mL of the prethermostated solvent mixture to give a final substrate concentration of about 1 mM. The reaction flask was sealed with a gastight PTFE septum and placed in a thermostated aluminum block in the HPLC apparatus. At appropriate intervals, samples were automatically injected onto the column and analyzed. The rate constants for the disappearance of the substrates were calculated from plots of substrate peak area versus time by means of a nonlinear regression computer program. The kinetics of 1-OH was also studied by UV spectrophotometry by following the increase in absorbance at 246 nm. Very good pseudo-first-order behavior was observed for all the reactions studied.

The separate rate constants for the reaction of **1-OMe** (Scheme 2 and Figure 1) were derived by computer simulation (least-squares fit) based upon the product composition data,

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which were obtained from the HPLC peak areas and the relative response factors, and the kinetic and equilibrium data of the alcohols. The small amount of the rearranged ether 2-OMe was not included in the simulation.

When starting from pure 1-OMe, the concentrations of 1-OMe, 1-OH, and 2-OH are described by the following equations:26

mol % **1-OMe** =
$$100e^{-m_1 t}$$
 (5)

mol % **1-OH** = $100(k_{CB}/m_2)(1 - e^{-m_2 t}) + 100\{(k_{AB} - k_{CB})/(1 - e^{-m_2 t}) + 100(k_{AB} - k_{CB})/(1 - e^{-m_2 t})\}$ $(m_2 - m_1)$ $(e^{-m_1t} - e^{-m_2t})$ (6)

$$mol \% 2-OH = 100 - mol \% 1-OMe - mol \% 1-OH$$
 (7)

where $m_1 = k_{AB} + k_{AC}m_2 = k_{BC} + k_{CB}$

Solvolysis in ¹⁸O-Labeled Water. The reaction medium was 50% aqueous acetonitrile prepared by mixing 150 μ L of labeled water with the same volume of an acetonitrile solution of the substrate 1-OMe and 0.1 μ L of 98% sulfuric acid. The reactions were run at room temperature (ca. 22 °C) in 2 mL GC autosampler vials sealed with PTFE septa. Aliquots (2 μ L) were injected at appropriate intervals directly onto the GC/ MS column. All components were well separated. The products 1-OH and 2-OH were detected and analyzed (30 eV) under "positive ion/full mass" mode as well as with electron impact and chemical ionization mode, respectively. For comparison, the same procedure was applied to the reaction of 1-OMe in unlabeled water/acetonitrile. Full incorporation of the labeled oxygen in the products 1-OH and 2-OH was found.

The relative abundance of ions (in % of the reference base peak m/z 105) in analysis of 1-OH were as follows: m/z 148 (M^+) 0.7%, m/z 150 (M^+) 17.3%, m/z 147 $([M - H]^+)$ 1.1%, m/z149 ($[M - H]^+$) 13.0%, m/z 133 ($[M - CH_3]^+$) 3.6%, m/z 135 $([M - CH_3]^+)$ 60.6%. For reaction in unlabeled water, the following values (recorded in the same order) were measured: 15.4%, 0.2%, 12.2%, 1.3%, 56.9%, 0.7%.

Computational Methods. Geometry optimization was carried out using the B3LYP combination of the Becke's three-

parameter hybrid functional (B3)27 for exchange and the Lee-Yang–Parr (LYP) gradient corrected correlation functional.²⁸ The 6-31G(d) valence double- ζ basis set of Pople and Hariharan was used.²⁹ Atomic charges were calculated using natural population analysis,³⁰ and nonspecific solvent interaction was considered by the self-consistent reaction field model of Tomasi and co-workers.³¹ All calculations were done with the Gaussian98 program package.32

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Supporting Information Available: Tables of absolute energies and atomic coordinates from B3LYP/6-31G(d) geometry optimization. This material is available free of charge via the Internet at http://pubs.acs.org.

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