J. Org. Chem. **1989**, *54*, 4899–4902

Comparative Substituent Effects of Tosyloxy, Benzoyloxy, and Phosphoryloxy Substituents in Carbocation Formation. Acid-Catalyzed Hydration of Vinyl Tosylates, Benzoates, and 1,1-Ditosylates

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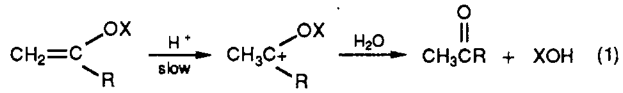
Received April 12, 1989

Kinetic results for the acid-catalyzed hydration of alkenyl esters $CH_2{=}C(OX)R$ (X = Bz, Ts) and literature data for X = Ac and PO_3Et_2 are analyzed by the excess acidity method, and it is concluded that all the substrates react by the $A_{SE}2$ mechanism of rate-limiting proton transfer to the double bond. Average substituent parameters σ_p^+ derived for the groups OBz, OAc, and OPO_3Et_2 of −0.18, −0.16, and −0.20, respectively, are similar and indicate these groups are modestly effective electron donors, while the average value of 0.08 for the OTs group indicates this to be a net electron withdrawing group. Hydrolysis of $t\text{-BuCH}{=}C(OTs)_2$ requires much stronger acid; it has $k_{H^+}/k_{D^+} = 5.75$ and a low slope of the rate versus acidity plot that is interpreted in terms of rate-limiting protonation of a substrate whose basic oxygens interact strongly with the acid solvent.

Esterification is known to diminish the electron-donor power of the hydroxy group. Thus for the HO group the value of the Brown-Hammett σ_p^+ parameter,[1] which is the most widely used measure of the ability of a group to stabilize a developing positive charge by π and σ donation, is −0.92, while those for the CH_3CO_2 (acetoxy) group and the $(EtO)_2PO_2$ (diethyl phosphoryloxy) group are −0.065, and −0.127, respectively.[2,3]

These σ_p^+ parameters can be used to quantatively account for reactivities in a diverse group of processes involving carbocations. For example in the acid-catalyzed hydration of enol derivatives proceeding with rate-limiting proton transfer (eq 1), the σ_p^+ parameters for HO (−0.92) and CH_3O (−0.78) and eq 2[4] accurately predict the greater reactivity of enols compared to enol ethers.[5] Thus in this case the σ_p^+ parameters derived from solvolytic reactivities are applicable to substituent effects in addition reactions.



(1)

$$\log k_{H^+} = -10.5\sum\sigma_p^+ - 8.92 \qquad (2)$$

There are exceptions to the ability of eq 2 to quantitatively predict alkene reactivities, even though the trends are usually properly indicated. In a particularly pertinent exception vinyl acetates are experimentally found to be more reactive toward aqueous acid than vinyl phosphates, contrary to what is predicted by the σ_p^+ parameters.[2a] One factor that may contribute to the discrepancy in this case is electrophilic interaction of the acidic solvent with the substituents.[6]

Recently we have engaged in the study of the reactivity of alkynyl tosylates, benzoates, and diethyl phosphates **1**.[7] These compounds are interpreted as reacting in acid by the $A_{SE}2$ mechanism of rate-limiting proton transfer to the triple bond (eq 3).[7]

$$\underset{\mathbf{1}}{RC{\equiv}COX} \xrightarrow[\text{slow}]{H^+} RCH{=}\overset{+}{C}OX \xrightarrow{H_2O} RCH_2CO_2H + HOX \qquad (3)$$

1a (X = Ts); **1b** (X = Bz,COC_6H_5); **1c** (X = PO_3Et_2)

It is desirable to compare the reactivities of the alkynyl derivatives **1** with the corresponding alkenyl esters reacting by eq 1. However, although the acid-catalyzed reactivity of alkenyl phosphates[2a,8] and acetates[2a,9] have been thoroughly studied, there is only inconclusive data on alkenyl benzoates[10] and none on alkenyl tosylates, although these latter compounds have been examined as precursors of vinyl cations.[11]

Some substituent parameters of the tosylate group have been measured,[12] but while the σ_p constant for this group of 0.29 indicates it is a rather strong electron-withdrawing group, the σ_R constant for tosylate of −0.21 indicates it can act as a resonance donor and indeed this group is deactivating toward electrophilic aromatic substitution but ortho–para directing.[12]

A value for σ_p^+ of −0.17 for benzoyloxy (BzO) has been estimated from data on chlorination of some disubstituted benzenes,[13] and this is almost exactly that of −0.19 for AcO

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Table I. Rates of Hydration of Alkenes in Aqueous H_2SO_4

alkene	$[H_2SO_4]$, M	X	k_ψ,[a] s^{-1}	$\log k_\psi - \log C_{H^+}$
$CH_2{=}C(OBz)Ph$[b]	7.72	2.602	6.44×10^{-2}	−2.168
2	7.43	2.480	5.31×10^{-2}	−2.238
	7.20	2.384	3.80×10^{-2}	−2.374
	6.53	2.111	2.47×10^{-2}	−2.520
	6.17	1.967	1.79×10^{-2}	−2.638
	5.40	1.644	6.57×10^{-3}	−3.016
	4.49	1.317	1.82×10^{-3}	−3.496
	3.53	0.790	4.70×10^{-4}	−3.980
$CH_2{=}C(OTs)Ph$[c]	9.30	3.306	1.01×10^{-1}	−2.042
3	8.55	2.962	2.47×10^{-2}	−2.624
	8.05	2.743	1.23×10^{-2}	−2.903
	7.72	2.602	5.76×10^{-3}	−3.216
	7.45	2.488	4.00×10^{-3}	−3.364
	7.20	2.384	2.70×10^{-3}	−3.520
	6.16	1.963	6.50×10^{-4}	−4.078
	5.15	1.567	2.28×10^{-4}	−4.457
$CH_2{=}C(OTs)CH_3$[d]	9.30	3.306	8.18×10^{-2}	−2.132
4	9.17	3.245	6.14×10^{-2}	−2.252
	8.55	2.962	2.56×10^{-2}	−2.608
	8.05	2.743	1.15×10^{-2}	−2.934
	7.45	2.488	4.03×10^{-3}	−3.360
	6.16	1.963	8.39×10^{-4}	−3.966
	5.15	1.567	3.31×10^{-4}	−4.295
t-$BuCH{=}C(OTs)_2$[e]	15.55	7.204	0.122	−2.075
5	14.41	6.389	4.37×10^{-2}	−2.517
	13.36	5.657	1.49×10^{-2}	−2.978
	12.34	4.984	5.33×10^{-3}	−3.406
	11.08	4.227	1.72×10^{-3}	−3.866
	15.12[f]	6.896	1.41×10^{-2}	−2.997
	14.02[f]	6.114	4.84×10^{-3}	−3.472
$CH_2{=}C(OAc)CH_3$[g]	46.49[h]	2.077	5.96×10^{-2}	−2.133
6	37.97[h]	1.498	1.19×10^{-2}	−2.724
	29.84[h]	1.029	2.92×10^{-3}	−3.206
	20.26[h]	0.583	7.63×10^{-4}	−3.584
	12.58[h]	0.308	2.54×10^{-4}	−3.824
	5.82[h]	0.122	8.15×10^{-5}	−3.952
$CH_2{=}C(OAc)Ph$[i]	45.45[h]	2.001	1.90×10^{-2}	−2.616
7	40.29[h]	1.647	6.24×10^{-3}	−3.037
	36.30[h]	1.395	2.95×10^{-3}	−3.306
	29.61[h]	1.017	9.53×10^{-4}	−3.687
	20.14[h]	0.578	2.60×10^{-4}	−4.049
	12.18[h]	0.295	1.04×10^{-4}	−4.196
	5.67[h]	0.118	3.44×10^{-5}	−4.314
$CH_2{=}C(OPO_3Et_2)Ph$[j]	31.84[h]	1.137	1.41×10^{-3}	−3.556
8	28.49[h]	0.959	7.25×10^{-4}	−3.786
	25.00[h]	0.789	4.07×10^{-4}	−3.967
	21.35[h]	0.628	2.03×10^{-4}	−4.187
	17.52[h]	0.477	1.01×10^{-4}	−4.389
	13.50[h]	0.337	5.17×10^{-5}	−4.550

[a] At least duplicate runs at each acidity, reproducibility ±5%, 25 °C. [b] Slope = 1.287 ± 0.025; intercept = −5.197 ± 0.042; k_{H^+} = (6.35 ± 0.61) × 10^{-6} s^{-1} (based on data for 3.53 to 6.53 M H_2SO_4 only). [c] Slope = 1.610 ± 0.028; intercept = −7.370 ± 0.079; k_{H^+} = (4.27 ± 0.78) × 10^{-8} s^{-1} (based on data from 7.20 to 9.30 M H_2SO_4 only). [d] Slope = 1.465 ± 0.028; intercept = −6.976 ± 0.083; k_{H^+} = (1.06 ± 0.20) × 10^{-7} s^{-1} (based on data from 7.45 to 9.30 M H_2SO_4 only). [e] Slope = 0.6061 ± 0.0055; intercept = −6.418 ± 0.033; k_{H^+} = (3.82 ± 0.29) × 10^{-7} s^{-1}; k_H/k_D = 5.75 ± 0.65. [f] $[D_2SO_4]$, M. [g] Reference 9c. Slope = 1.024 ± 0.002; intercept = −4.259 ± 0.003, k_{H^+} = (5.51 ± 0.04) × 10^{-5} s^{-1} (based on data from 29.84 to 46.49% H_2SO_4 only). [h] % H_2SO_4 (w/w). [i] Reference 9d. Slope = 1.173 ± 0.017; intercept = −4.996 ± 0.026; k_{H^+} = (1.01 ± 0.06) × 10^{-5} s^{-1}. [j] Reference 8c. Slope = 1.174 ± 0.053; intercept = −4.910 ± 0.041; k_{H^+} = (1.23 ± 0.12) × 10^{-5} s^{-1}.

obtained from chlorination data of acetoxybenzene.[2b]

Because of the importance of alkenyl tosylates and benzoates we have accordingly undertaken a study of the reactions of compounds **2**–**5** in acid.

$CH_2{=}C(OBz)Ph$ **2** $CH_2{=}C(OTs)Ph$ **3**

$CH_2{=}C(OTs)CH_3$ **4** t-$BuCH{=}C(OTs)_2$ **5**

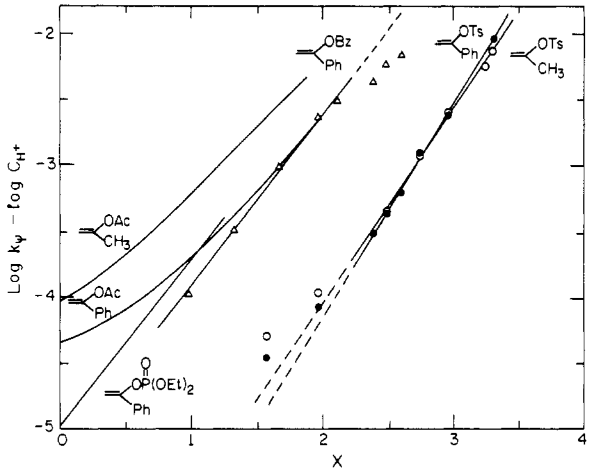

Figure 1. Reactivity vs excess acidity X for vinyl benzoates, acetates, and tosylates.

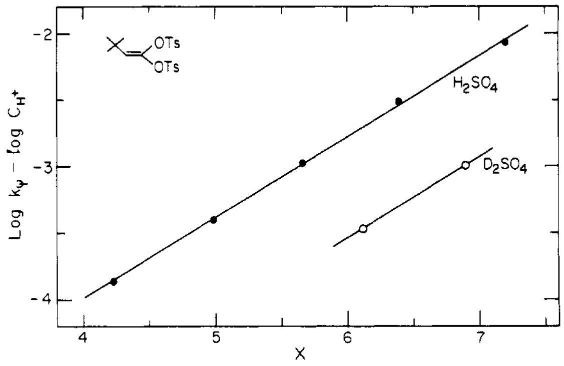

Figure 2. Reactivity vs excess acidity X for **5**.

Table II. Comparative Reactivity of Vinyl Esters

substrate	k_{H^+},[a] s^{-1}	$\sigma_p^+(OX)$
$CH_2{=}C(OBz)Ph$, **2**	6.35×10^{-6}	−0.18
$CH_2{=}C(OTs)Ph$, **3**	4.27×10^{-8}	0.03
$CH_2{=}C(OTs)CH_3$, **4**	1.06×10^{-7}	0.12
t-$BuCH{=}C(OTs)_2$, **5**	3.82×10^{-7}	
$CH_2{=}C(OAc)CH_3$, **6**	5.51×10^{-5}	−0.13
$CH_2{=}C(OAc)Ph$, **7**	1.01×10^{-5}	−0.19
$CH_2{=}C(OPO_3Et_2)Ph$, **8**	1.23×10^{-5}	−0.20

[a] 25 °C.

Results

1-(Benzoyloxy)-1-phenylethene (**2**) was prepared by the reaction of $CH_2{=}C(OSiMe_3)Ph$ with benzoic anhydride catalyzed by $HgCl_2$.[14] The alkenyl tosylates **3**[15] and **4**[15] were obtained by generation of the enolates from the corresponding ketones with i-Pr_2NLi and reaction with toluenesulfonic anhydride (eq 4). 1,1-Bis(tosyloxy)-3,3-dimethylbutene (**5**) was reported previously.[16]

$$CH_3C(O)R \xrightarrow[2.\ Ts_2O]{1.\ i\text{-}Pr_2NLi} CH_2{=}C(OTs)R \qquad (4)$$

The hydration kinetics of **2**–**5** in aqueous H_2SO_4 were measured by observing the change in the UV absorption of the substrates and are reported in Table I. The dependence of the rates on acidity was analyzed by the excess acidity scale X,[17] as were literature data on $CH_2{=}C(O$-

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Ac)CH_3 (**6**),[9c] $CH_2{=}C(OAc)Ph$ (**7**),[9d] and $CH_2{=}C(OPO_3Et_2)Ph$ (**8**),[8c] as compiled in Table I. Plots of log k_ψ − log C_{H^+} vs X[18] are shown in Figures 1 and 2. As noted in Table I certain points deviating from the linear correlations were excluded from the data analysis. Table II contains the derived standard state k_{H^+} and σ_p^+ values.

The UV spectra of the products of the reactions of **2**–**4** matched those of the corresponding ketone and acid, indicating these esters were reacting as shown in eq 5. The alkene absorption for **5** disappeared during the reaction and the ^1H NMR spectrum of the product matched that of a mixture of the corresponding acids, indicating reaction as in eq 6.

$$CH_2{=}C(OBz)R \text{ or } CH_2{=}C(OTs)R \xrightarrow{H_3O^+} CH_3C(O)R + BzOH \text{ or } TsOH \quad (5)$$

$$t\text{-}BuCH{=}C(OTs)_2 \xrightarrow{H_3O^+} t\text{-}BuCH_2CO_2H + 2TsOH \quad (6)$$

Discussion

As shown in Figure 1 the reactivities and rate dependence on acidity of the alkenyl tosylates $CH_2{=}C(OTs)Ph$ (**3**) and $CH_2{=}C(OTs)CH_3$ (**4**) are remarkably similar, with a slightly greater slope for **3** (1.610 vs 1.465) and a slightly greater k_{H^+} derived for **4** (k_{rel} **4**/**3** = 2.6). The rate versus acidity profiles for **3** and **4** are also very similar to those for $CH_2{=}C(OAc)Ph$ (**7**)[9d] and $CH_2{=}C(OPO_3Et_2)Ph$ (**8**),[8c] compounds established to react by the Ad_E2 mechanism of rate-limiting proton transfer to the alkene (eq 1), and this evidence establishes that this pathway holds for **3** and **4** as well.

The modest deviations of the points at lower acidity for **3** and **4** from the linear correlations (Figure 1) may indicate the intervention of some hydrolysis of these tosylates involving S–O bond cleavage, much as similar behavior for **6**[9c] and **7**[9d] was interpreted in terms of acyl–oxygen bond cleavage. However, this pathway of tosylate hydrolysis in strong acid has not been thoroughly elucidated,[19b] and because the current data set is rather limited, this mechanistic assignment cannot be made with confidence.

The near identity of the reactivity of **3** and **4** shown in Figure 1 contrasts with the reactivity of $CH_2{=}C(OAc)CH_3$ (**6**)[9c] and $CH_2{=}C(OAc)Ph$ (**7**),[9d] where the former is more reactive by a factor of 5.5. This latter reactivity order agrees qualitatively with the σ_p^+ values of −0.31 for CH_3 and −0.19 for Ph,[1] which predict methyl to be a better donor than phenyl toward positive charge. However the relative effects of these groups in alkene protonations are highly variable, as documented in a variety of cases.[4] These variations may arise from conformational and ground-state effects, and the reactivities of **3** and **4** are one more example of this imperfectly understood system.

The tosylates **3** and **4** are less reactive than the other alkenes in Figure 1 by factors as large as 290 for the comparison of **3** to $CH_2{=}C(OPO_3Et_2)Ph$ (**8**). Greater electron-withdrawing ability for tosylate relative to acetate, benzoate, and diethyl phosphate is expected so this reactivity order is reasonable. Application of eq 2 to k_{H^+} for **3** and **4** to derive σ_p^+ values for OTs gives 0.032 for $CH_2{=}C(OTs)Ph$ (**3**) and 0.123 for $CH_2{=}C(OTs)CH_3$ (**4**), or an average value of 0.078.

The linear portion of the rate vs acidity plot for $CH_2{=}C(OBz)Ph$ (**2**) coincides with that for $CH_2{=}C(OAc)Ph$ (**7**) at the highest acidities examined for the latter, which is interpreted as reacting by the Ad_E2 mechanism (eq 1) at this acidity.[9d] The similarity in the reactivity in **2** and **7** is matched by the similarity of the σ_p^+ values for OAc[2b] and OBz[12b] (−0.19 and −0.13, respectively) derived from arene chlorination. Rate vs acidity plots for **2** and $CH_2{=}C(OPO_3Et_2)Ph$ (**8**) are also essentially parallel, and their reactivities are very similar (k_{rel} **8**/**2** = 1.9). The acid hydration of **8** is also interpreted in terms of the Ad_E2 mechanism, and these comparisons of **2** to **7** and **8** establish this mechanism for the former as well. Application of eq 2 to the data for **2** gives a σ_p^+ value of −0.18 for the benzoyloxy group, essentially identical with both the value of −0.17 derived from arene chlorination and the value of −0.19 derived for OAc from acid hydration of $CH_2{=}C(OAc)Ph$ (**7**). However as noted above[2,3] the σ_p^+ for OAc derived from cumyl chloride solvolysis differs from that obtained by alkene hydration and chlorination.

At lower acidities the reactivity of $CH_2{=}C(OAc)Ph$ (**7**) exceeds that expected for the Ad_E2 pathway, a result attributed[9d] to competing $A_{Ac}2$ hydrolysis of this substrate, which is consistent with our analysis. A corresponding deviation for $CH_2{=}C(OBz)Ph$ (**2**) is not observed, suggesting a lower susceptibility of this substrate to $A_{Ac}2$ reaction. At higher acidities the points for **2** deviate below the line predicted, and we attribute this result to hydrogen bonding[6] or equilibrium protonation[20] interactions of the acidic solvent with the basic oxygens of the benzoate reducing the donor ability of this group. We have observed both of these phenomena previously with other groups.[6,20]

In contrast to the results for alkenyl esters, which show an order of reactivity for k_{H^+} of OPO_3Et_2 > OBz > OTs the alkynyl tosylate $CH_3C{\equiv}COTs$ (**1a**) is more reactive than the corresponding benzoate, and the phosphate is the least reactive of the group. The reason for this reversal in substituent effects is not apparent, but a highly speculative interpretation is that ground-state effects are more important in the alkynyl esters and that the alkynyl tosylate with a strongly electron withdrawing tosylate group attached to the electronegative sp hybridized carbon of the alkyne has a high ground-state energy and high reactivity.

The behavior of t-$BuCH{=}C(OTs)_2$ (**5**) differs from that of $CH_2{=}C(OTs)Ph$ (**3**) and $CH_2{=}C(OTs)CH_3$ (**4**), in that **5** requires much stronger acids for hydration to be experimentally observable and also has a much lower dependence of rate on acidity than do the two monotosylates. Thus extrapolated rates for **3** exceed those measured for **5** by factors of 240 and 930 in 9.30 and 11.08 M acids, while **4** is 220 and 660 times more reactive in the same acids. The different dependence of the rates on the acidity leads to large variations in the rate ratios and precludes meaningful derivation of σ_p^+ values for OTs based on **5**, but the low donor power of the OTs group manifested in $CH_2{=}C(OTs)CH_3$ and $CH_2{=}C(OTs)Ph$ is also displayed by the second tosylate group. The *tert*-butyl group in t-$BuCH{=}C(OTs)$ is not expected to cause the low reactivity of this substrate.[21]

The low slope for t-$BuCH{=}C(OTs)_2$ (**5**) in Figure 1 is evidently due to the same cause proposed for the deviations for **2**, namely protonation of the basic oxygens of the substrate.[6,20] Such behavior for tosylates in strong H_2SO_4 has been noted previously.[19b] The solvent isotope k_{H^+}/k_{D^+}

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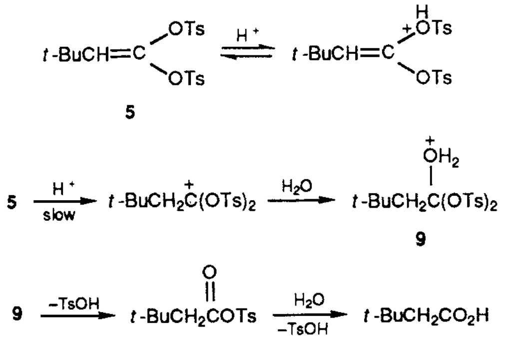
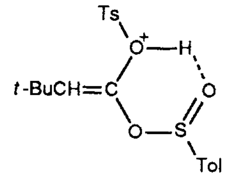
Scheme I



for this substrate of 5.75 ± 0.65 indicates that the rate-limiting step is proton transfer to the double bond, although it is not clear whether this involves protonated or unprotonated alkene (Scheme I). The isotope effect excludes an alternative mechanism involving S–O bond cleavage such as was observed for $(CF_3)_2CHOTs$[19a] and t-$BuCH_2OTs$.[19c,d]

The O-protonated form of **5** could be stabilized by an intramolecular hydrogen bond but there is no direct evidence for this.



In summary, vinyl benzoates, acetates, and phosphates display a modest enhancement in their reactivity toward protic acid induced by the ester substituents compared to hydrogen, whereas vinyl tosylates are less reactive and the tosylate group is no better than hydrogen at activating the double bond. 1,1-Bis(tosyloxy)alkenes are deactivated even further.

Experimental Section

Infrared spectra were obtained on a Nicolet 5 DX FT-IR spectrometer. ^{1}H NMR spectra were recorded in $CDCl_3$ solutions using a Varian T-60 spectrometer and are reported as δ units (ppm downfield from TMS). UV spectra were recorded in acetonitrile using a Hewlett-Packard 8451A diode array spectrophotometer.

Materials. Triethylamine and diisopropylamine were distilled from KOH. Trimethylsilyl chloride was dried over calcium hydride and distilled immediately prior to use. Acetophenone, n-BuLi, benzoyl chloride, and p-toluenesulfonic anhydride were obtained from Aldrich Chemical Co. and used without further purification.

α-[(Trimethylsilyl)oxy]styrene. To 31.2 mL (50 mmol) of n-BuLi (1.6 M in hexanes) was added 7.00 mL (50 mmol) of diisopropylamine in 50 mL of dry THF at −78 °C under nitrogen, and acetophenone (5.83 mL, 50 mmol) in THF (30 mL) was then added slowly at −78 °C and left to stir for 30 min. Then a mixture of trimethylsilyl chloride (32 mL) and triethylamine (35 mL) was added via a filter stick, and the resulting slurry was allowed to warm to room temperature and stirred for 12 h. The volatiles were removed in vacuo, 100 mL of pentane was added, and the solution was filtered. The solvent was evaporated, and bulb-to-bulb distillation afforded 6.18 g (64%) of product as a clear, colorless liquid: ^{1}H NMR δ 0.30 (s, 9, Me_3Si), 4.20 (d, 1 J = 2 Hz)8 4.65 (d, 1, J = 2 Hz), 7.20 (m, 5 H).

α-(Benzoyloxy)styrene (2). A mixture of 5.00 g (26 mmol) of α-[(trimethylsilyl)oxy]styrene, 3.65 g (26 mmol) of benzoyl chloride, and 200 mg of $HgCl_2$ was heated 2 h at 100 °C. After cooling, ether and water were added, and then pyridine was added until no further turbidity was observed. The layers were separated, the aqueous layer was washed with ether, and the combined organic layers were washed, in succession, with 10% HCl, saturated sodium bicarbonate, and brine and dried ($MgSO_4$). The solvent was removed in vacuo to leave a red-brown oil, which was purified by flash chromatography using silica gel with 60/40 CH_2Cl_2/hexanes to give **2** (4.23 g, 16.8 mmol, 72%) as a yellow-green oil: ^{1}H NMR δ 5.15 (d, 1, J = 3 Hz), 5.55 (d, 1, J = 3 Hz), 7.40 (m, 8 H), 8.20 (m, 2 H); IR (cm^{-1}) ν_{max} 1742, 1643, 1241; UV (CH_3CN) (nm) λ_{max} 236 (ϵ 12 400), 272 (ϵ 1800).

α-(Tosyloxy)styrene (3). Acetophenone (0.50 mL, 4.3 mmol) in 2 mL of THF was slowly added to 5.00 mmol of freshly prepared LDA at −78 °C and stirred for 1 h. The resulting pale yellow solution was transferred to a solution of 3.0 g (9.2 mmol) of toluenesulfonic anhydride in 20 mL of THF at 0 °C via a double-tip needle. This mixture was warmed to room temperature over a 3-h period and then poured into 200 mL of cold saturated $NaHCO_3$. Extraction into ether (250 mL) was followed by washing with brine (250 mL) and water (250 mL) and drying ($MgSO_4$). Evaporation of the solvent left a red-brown oil (0.94 g, 80% yield). Recrystallization from 20% ether/pentane gave bright yellow crystals of **3**, mp 48–50 °C: ^{1}H NMR δ 2.45 (s, 3), 5.10 (d, 1, J = 3 Hz), 5.35 (d, 1, J = 3 Hz), 7.50 (m, 9); UV (CH_3CN) nm λ_{max} 230 (ϵ 18 000), 249 (ϵ 13 000), 263 (ϵ 500).

2-(Tosyloxy)propene (4). Acetone 0.31 mL (4.3 mmol) was added to 5.0 mmol of freshly prepared LDA at −78 °C, and this yellow solution was added to toluenesulfonic anhydride (3.00 g, 9.2 mmol) in 20 mL of THF at 0 °C and left to warm to room temperature over 5 h and then worked up as above. Bulb-to-bulb distillation followed by low-temperature crystallization from ether/pentane afforded 300 mg of **4** (33%): ^{1}H NMR δ 1.80 (s, 3, vinyl CH_3), 2.40 (s, 3, aryl CH_3), 4.60 (s, 2, $C{=}CH_2$), 7.45 (m, 5); UV (CH_3CN) λ_{max} (nm) 230 (ϵ 10 000), 265 (ϵ 550).

Kinetics. The UV kinetic measurements were made with Cary 118 and Cary 210 spectrometers, with chamber temperature of 24.6 ± 0.2 °C. Kinetics for hydrolysis of compounds **2**, **3**, **4**, and **5** were measured by following the decrease in absorption at 243, 232, 227, and 242 nm, respectively for 8–10 half-lives. A typical run involved injection 10 μL of a 0.05 M solution of substrate in acetonitrile into 3 mL of sulfuric acid. Total absorbance changes were approximately 0.1 absorbance unit, except for compound **5** where the change in absorbance was about 1 unit.

Product Studies. A mixture of 1,1-bis(tosyloxy)-3,3-dimethylbutene (**5**)[16] (40 mg, 0.09 mmol) in 3 mL of 14.4 M H_2SO_4 became homogeneous on warming to 60 °C for 10 min and gave the same ^{1}H NMR spectrum as an authentic 1:2 mixture of 3,3-dimethylbutanoic acid and toluenesulfonic acid in 14.4 M H_2SO_4. The solution was diluted with H_2O and extracted with ether, and after drying and evaporation of the ether layer the residue gave the same ^{1}H NMR spectrum in $CDCl_3$ as the authentic products.

The UV spectra of reaction products in acid from the kinetic measurements on **2**–**5** matched those expected according to eq 5 and 6 and were assigned as follows: **2**, λ_{max} 258 nm (ϵ 10 000), $PhCO_2H$, λ_{max} 294 nm (ϵ 11 000), $PhCOCH_3$; **3**, λ_{max} 226 nm (ϵ 10 000), TsOH; λ_{max} 294 nm (ϵ 11 000), $PhCOCH_3$; **4** and **5**, λ_{max} 226 nm (ϵ 10 000), TsOH.

Acknowledgment. Financial support by the donors of the Petroleum Research Fund, administered by the American Chemical Society, by the Natural Sciences and Engineering Research Council of Canada, and by the National Cancer Institute of the National Institutes of Health (Grant IROCA16903) is gratefully acknowledged.