Me), 1.89 (s, 6, 2 Me), 4.21 (m, 4, 2 OCH_2), and 7.34 (quartet, 4, aryl)); and diethyl *m*-phosphoryloxycumyl chloride (**8**) (NMR ($CDCl_3$) δ 1.34 (t, 6, $J_{H-H} = 7$, $J_{P-H} = 1$ Hz, 2 Me), 1.96 (s, 6, 2 Me), 4.23 (m, 4, 2 OCH_2), and 7.3 (m, 4, aryl)).

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Research Council of Canada, the National Institute of General Medical Sciences, and the Undergraduate Research Fund of Scarborough College for support of this work. We thank Professor de la Mare for supplying the unpublished data in ref 11c.

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Acid-Catalyzed Hydration of 1,2-Disubstituted Alkenes

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Abstract: *cis*- and *trans*-1,2-dicyclopropylethylene are protonated by aqueous acid at rates 5.6×10^5 and 1.4×10^6, respectively, times slower than their isomer 1,1-dicyclopropylethylene. *cis*- and *trans*-1-cyclopropylpropene are protonated at rates 3.2×10^3 and 7.4×10^3, respectively, times slower than the isomeric 2-cyclopropylpropene. The rate effects show that the position of the proton in the transition state is highly unsymmetrical relative to the double bond, corresponding to the $A_{SE}2$ mechanism of rate-determining proton transfer to carbon. The effect of the substituent on the β carbon undergoing protonation can be accounted for by consideration of the electron-donating ability of the substituent in the transition state and the effect of the substituent on the ground state stability of the olefin. The rates of the 1,2-disubstituted alkenes are quantitatively correlated by the equation $\log k_2 = -12.3[\sigma_p^+ + 0.60(\sigma_m^+ + 0.08D - 0.084)] - 10.1$ where σ_p^+ and σ_m^+ are the electrophilic substituent constants for the α and β substituents, respectively, and D is the double bond stabilization parameter for the β substituent.

In previous work in this laboratory[1] the rates of acid-catalyzed hydration of 1,1-disubstituted alkenes (eq 1) were found to be correlated with σ_p^+ parameters of the substituents R by eq 2. These results confirmed that these compounds were reacting by the $A_{SE}2$ mechanism with rate-determining protonation on carbon giving a stabilized carbonium ion.

$$R_2C{=}CH_2 \xrightarrow[\text{slow}]{H^+} R_2\overset{+}{C}CH_3 \xrightarrow{H_2O} R_2COHCH_3 \qquad (1)$$

$$\log k_2 = -12.3\Sigma\sigma_p^+ - 10.1 \qquad (2)$$

It appeared that the extension of our analysis to hydration of alkenes substituted on both carbons of the double bond would be informative. Previous correlations[1,2] of hydration data have not included such alkenes, and other electrophilic additions for which such treatments have been reported often involve fewer compounds, suffer from mechanistics complications such as bridging, and cover small ranges of reactivity.[2] It would seem particularly worthwhile to develop a consistent picture of the effect of substituents on both the 1 and 2 positions of alkenes in protonations as this is conceptually the simplest

Table I. Rates of Hydration of 1,2-Disubstituted Alkenes in Aqueous Acid at 25 °C

Alkene	H_2SO_4, M[a]	H_2SO_4, %[b]	H_0	H_R	k_{obsd}, s^{-1}[c]	Log k
c-PrCH=CH-c-Pr	1.92	16.9	−0.81	−1.55	1.76×10^{-4}	−3.76
(cis)	2.37	20.4	−1.03	−1.98	3.39×10^{-4}	−3.47
73	2.98	24.8	−1.38	−2.54	6.84×10^{-4}	−3.16
	3.85	30.8	−1.78	−3.36	2.39×10^{-3}	−2.62
	4.33	33.9	−1.98	−3.82	4.40×10^{-3}	−2.36
c-PrCH=CH-c-Pr	1.92	16.9	−0.81	−1.55	6.81×10^{-5}	−4.17
(trans)	2.37	20.4	−1.03	−1.98	1.18×10^{-4}	−3.93
72	2.98	24.8	−1.38	−2.54	2.48×10^{-4}	−3.61
	3.85	30.8	−1.78	−3.36	8.75×10^{-4}	−3.06
	4.33	33.9	−1.98	−3.82	1.49×10^{-3}	−2.83
c-PrCH=CHMe	0.500	4.8	0.13	0.03	4.26×10^{-5}	−4.37
(cis)	1.92	16.9	−0.79	−1.55	5.60×10^{-4}	−3.25
71	2.37	20.4	−1.03	−1.98	1.15×10^{-3}	−2.94
	2.98	24.8	−1.38	−2.54	2.61×10^{-3}	−2.58
	3.85	30.8	−1.78	−3.36	8.64×10^{-3}	−2.06
	4.33	33.9	−1.98	−3.82	1.31×10^{-2}	−1.88
c-PrCH=CHMe	1.92	16.9	−0.81	−1.55	2.31×10^{-4}	−3.64
(trans)	2.37	20.4	−1.03	−1.98	4.08×10^{-4}	−3.39
70	2.98	24.8	−1.38	−2.54	9.60×10^{-4}	−3.02
	3.85	30.8	−1.78	−3.36	2.89×10^{-3}	−2.54
	4.33	33.9	−1.98	−3.82	4.86×10^{-3}	−2.31

[a] Determined by titration. [b] Calculated from molarity using standard tables. [c] Average of at least two runs.

Table II. Isotope Effects on Acid-Catalyzed Hydration of 1,2-Disubstituted Alkenes

Alkene	k_{obsd} (3.85 M H_2SO_4), s^{-1}	k_{obsd} (3.80 M D_2SO_4), s^{-1}	k_H/k_D
c-PrCH=CH-c-Pr (cis)	2.39×10^{-3}	1.13×10^{-3}	2.1
c-PrCH=CH-c-Pr (trans)	8.75×10^{-4}	4.12×10^{-4}	2.1
c-PrCH=CHMe (cis)	8.64×10^{-3}	4.26×10^{-3}	2.0
c-PrCH=CHMe (trans)	2.89×10^{-3}	1.63×10^{-3}	1.8

of the electrophilic additions. There have been many studies of the effect of substituents in 1,2-substituted alkenes for other electrophilic additions such as brominations and oxymercurations, but the interpretation of these results is hampered by the lack of a thorough understanding of the effects of the substituents in hydrations, which appears to be a much simpler reaction.

It has been noted[3] that propene and the isomeric 2-butenes undergo hydration at similar rates, and it was stated that this "probably represents opposing effects of a small steric retardation and a small general inductive acceleration". In studies of protonation of β-arylalkenes the β-substituent effect was attributed to transition state electronic factors[4] or ground state stabilization.[5] It was desirable to make a quantitative assessment of these factors.

Accordingly we have undertaken the study of the rates of acid-catalyzed hydration of alkenes substituted on both ends of the double bond. Cyclopropylalkenes were chosen for study because the general utility of these substrates for mechanistic investigations[1] has already been established. Our goal was to establish the major structural effects on reactivity and if possible to quantitatively account for the behavior in terms of a simple theory based on well-established principles.

Results

Rates of hydration of nonterminal cyclopropylalkenes were measured by observation of the disappearance of the olefin absorption in the ultraviolet. Compounds examined were *trans*-1-cyclopropylpropene (**70**), *cis*-1-cyclopropylpropene (**71**), *trans*-1,2-dicyclopropylethylene (**72**), *cis*-1,2-dicyclopropylethylene (**73**), and tetracyclopropylethylene. The numbering of the compounds is in accord with the sequence we have used previously.[1] Rates for **70–73** in H_2SO_4 are given in Table I and rates in D_2SO_4 and calculated isotope effects are given in Table II.

The correlations of the rates with the acidity functions[6,7] H_0 and H_R were examined. The acidity functions were found to give equally good straight line behavior when log k_{obsd} was plotted against H_0 or H_R. The rates for tetracyclopropylethylene were of the same order of magnitude as **70–73** but showed appreciable random scatter. Presentation of the results for this compound are therefore deferred to a later date.

The log k values were extrapolated vs. H_0 to low acidity ($H_0 = 0.0$) for calculation of hydronium ion catalyzed rate constants, which are given in Table III, along with relative rate constants and cis/trans rate ratios. The choice of $H_0 = 0.0$ as the terminus of the extrapolation is based on the desire to approach relatively near the point where the H_0 and pH functions merge at low acidity, while minimizing the extrapolation from the range of the experimental determinations. This point is discussed in more detail in ref 1c. The data are correlated by the equation $\log k_{obsd} = \gamma H_0 + \epsilon$, and the values of γ and ϵ for each of the alkenes studied are included in Table III. All of the available rate data for hydration of acyclic, vicinally substituted alkenes in H_2O are collected in Table IV. There is another large body of data available for reactions in 80% dioxane–20% water, and there are five compounds for which rates are available in both solvent systems. Inasmuch as the rate ratios between the two solvent systems are nearly constant the rates in 80% dioxane were converted to rates in water by application of the average of the H_2O/80% dioxane factor for the compounds examined in both solvents. These data are collected in Tables V and VI.

Data are also available for the acid-catalyzed isomerization of *cis*-stilbenes (eq 3).[4]

$$cis\text{-ArCH=CHAr} \xrightarrow{H^+} \text{Ar}\overset{+}{\text{C}}\text{HCH}_2\text{Ar} \rightleftharpoons trans\text{-ArCH=CHAr} \quad (3)$$

Table III. Rates of Hydration of 1,2-Disubstituted Alkenes Extrapolated to $H_0 = 0.0$

Alkene	k_2, $M^{-1}\ s^{-1}$ [a]	k_{rel}	Cis/trans	γ [b]	ϵ [b]
c-PrCH=CH-c-Pr	1.90×10^{-5} (cis) **73**	0.075	2.5	−1.18	−4.72
	7.41×10^{-6} (trans) **72**	0.029		−1.15	−5.13
c-PrCH=CHMe	6.24×10^{-5} (cis) **71**	0.25	2.3	−1.19	−4.20
	2.71×10^{-5} (trans) **70**	0.11		−1.14	−4.57
$c\text{-}Pr_2C{=}CH_2$	10.6[c]	41 700			
$c\text{-}PrCH{=}CH_2$	2.54×10^{-4}[c]	1.0			
$c\text{-}PrCMe{=}CH_2$	0.200[c]	787			

[a] Derived from the equation in footnote *b* at $H_0 = 0.0$. [b] Constants in the equation $\log k_{obsd} = \gamma H_0 + \epsilon$, correlation coefficients 0.998, 0.997, 1.000, and 1.000, respectively. Constants in the equation $\log k_{obsd} = \gamma H_R + \epsilon$ are **73**, −0.62, −4.71, 1.000; **72**, −0.60, −5.12, 0.999; **71**, −0.66, −4.29, 0.998; **70**, −0.59, −4.55, 0.999; for γ, ϵ, and the correlation coefficients, respectively. [c] Reference 1a.

Table IV. β-Substituent Effects on Protonation of Alkenes, H_2O, 25 °C

	k_2, $M^{-1}\ s^{-1}$				k_{unsub}/k_{sub}	
Sub alkene	Cis	Trans	Unsub alkene	k_2, $M^{-1}\ s^{-1}$ (unsub)	Cis	Trans
c-PrCH=CHMe[a]	6.24×10^{-5}	2.71×10^{-5}	$c\text{-}PrCH{=}CH_2$	2.54×10^{-4}	4.1	9.4
EtOCH=CHMe[b]	0.476	0.159	$EtOCH{=}CH_2$[b]	1.76	3.7	11
MeOCH=CHMe[b]	0.254 (0.245)[k]	0.0724 (0.0818)[k]	$MeOCH{=}CH_2$[b]	0.762	3.0	11
$MeOCH{=}CMe_2$[k]		0.0252	MeOCH=CHMe[b]	0.254 (c) 0.0742 (t)	 2.9	10
MeCH=CHMe[c]	8.32×10^{-8}	3.51×10^{-8}	$MeCH{=}CH_2$[c]	4.95×10^{-8}	0.6[d]	1.4[d]
PhCH=CHMe[e,f]		1.12×10^{-7}	$PhCH{=}CH_2$[e]	(1.15×10^{-6})[e]		10
EtCH=CHEt[e]	1.78×10^{-7}	2.11×10^{-7}	$n\text{-}BuCH{=}CH_2$[e]	1.08×10^{-7}	0.61[d]	0.51[d]
$Me_2C{=}CHMe$[c]	2.15×10^{-4}		$Me_2C{=}CH_2$[c]	3.71×10^{-4}	1.7	
$(MeO)_2C{=}CMe_2$[g]	28.9		$(MeO)_2C{=}CH_2$[h,i]	1.5×10^{5}	5.2×10^{3}	
$MeOCH{=}CMe_2$[k]	0.0252		$MeOCH{=}CH_2$[b]	0.762	30	
MeOCMe=CHPh[j]	1.67		$MeOCMe{=}CH_2$[i,l]	2.26×10^{2}	135	
$(EtO)_2C{=}CHCl$[g]	1.5×10^{4}		$(EtO)_2C{=}CH_2$[h]	10^{6}	67	
c-PrCH=CH-c-Pr[a]	1.90×10^{-5}	7.41×10^{-6}	$c\text{-}PrCH{=}CH_2$	2.54×10^{-4}	13[d]	34[d]
$Me_2C{=}CMe_2$[m]	3.42×10^{-4}		$Me_2C{=}CH_2$[c]	3.71×10^{-4}	1.1[d]	
PhCH=CHPh[n]	6.36×10^{-10}	7.07×10^{-11}	$PhCH{=}CH_2$[o]	3.72×10^{-7}	585[d]	5.3×10^{3}[d]
MeOCH=CHEt[k]	0.333	0.0948	$MeOCH{=}CH_2$[b]	0.762	2.3	8.0

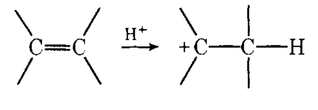
[a] This work. [b] D. S. Sagatys, Thesis, Illinois Institute of Technology, 1970. [c] Reference 3. Rates given are for *cis*- and *trans*-2-butene relative to propene of 1.68 and 0.71, respectively, and these were multiplied by the absolute rate for propene in ref 1a. The 2-methyl-2-butene rate calculated in this way from the data of Taft (2.49×10^{-4} $M^{-1}\ s^{-1}$) agrees well with the value here from H. J. Lucas and Y.-P. Liu, *J. Am. Chem. Soc.*, **56**, 2138 (1934). [d] These ratios are doubled if the rate of the vicinally symmetrically substituted compound is divided by a statistical factor of 2. [e] Rates for k_{obsd} in 48.7% H_2SO_4, K. Yates, G. H. Schmid, T. W. Regulski, D. G. Garratt, H.-W. Leung, and R. McDonald, *J. Am. Chem. Soc.*, **95**, 160 (1973), were converted to k_2 values by division by h_0 of 1.78×10^3. The rate for styrene differs from that given below, but is appropriate for this comparison under the same conditions. [f] Cis isomerizes to trans under these conditions. [g] T. S. Straub, Thesis, Illinois Institute of Technology, 1970. [h] A. Kankaanpera and H. Tuominen, *Suom. Kemistil. B*, **40**, 271 (1967). [i] Rate for $(EtO)_2C{=}CH_2$ converted by twice multiplying by the MeO/EtO factor 0.39. This factor is the average for the comparisons of ROCH=CHMe (cis and trans, Table V), $ROCH{=}CH_2$ (Table IV), and $ROCPh{=}CH_2$ (ref 1a). The rate for $MeOCMe{=}CH_2$ was obtained using the same factor. [j] Reference 5. [k] P. Salomaa and P. Nissi, *Acta Chem. Scand.*, **21**, 1386 (1967). [l] A. J. Kresge, H. L. Chen, Y. Chiang, E. Murrill, M. A. Payne, and D. S. Sagatys, *J. Am. Chem. Soc.*, **93**, 413 (1971). [m] Calculated by extrapolating the data of J. L. Jensen and D. J. Carré, *J. Org. Chem.*, **36**, 3180 (1971), to $H_0 = 0.0$. [n] Reference 4, see text. [o] From the data of J.-P. Durand, M. Davidson, M. Hellin, and F. Coussemant, *Bull. Soc. Chim. Fr.*, 52 (1966), for reactions in sulfuric acid extrapolated to $H_0 = 0.0$. For comparison the data of W. M. Schubert and B. Lamm, *J. Am. Chem. Soc.*, **88**, 120 (1966), for reaction in $HClO_4$ extrapolated to $H_0 = 0.0$ gives $k_2 = 9.96 \times 10^{-8}$ $M^{-1}\ s^{-1}$.

The rate-limiting step in these reactions is protonation of the double bond, and although the hydration product is formed in the course of the reaction it is present only to the extent of 1% at equilibrium in the case of stilbene.[4b] The protonation rate for *cis*-stilbene, and that derivable for *trans*-stilbene from the free energy diagram for the reaction,[4a] are included in Table IV.

The products and stereochemical course of the hydration of **70**–**73** are the subject of a separate study. The absorbance decreased by at least 80% during the course of each of the reactions, indicating a large equilibrium constant for hydration.

Discussion

A striking feature of the relative rate data in Table III is the 10^6-fold diminution in reactivity of the isomeric 1,2-dicyclopropylethylenes **72** and **73** over 1,1-dicyclopropylethylene. This enormous difference is a dramatic confirmation that the protonations occur by the $A_{SE}2$ mechanism of rate-determining proton transfer to carbon (eq 4). The dependence of the rates upon acidity and the solvent isotope effects are also in accord with this mechanism.



(4)

The 1-cyclopropylpropenes **70** and **71** are similarly less reactive than the isomeric 2-cyclopropylpropene by factors of 3000–7000. These facts further illustrate the highly unsymmetrical nature of the transition state, and the greatly different effects of substituents at the two ends of the double bond.

Table V. Correlation of Rates of Disubstituted Alkenes $R_\alpha CH{=}CHR_\beta$

R_α	R_β	$k(R_\alpha CH{=}CHR_\beta)^a/k(R_\alpha CH{=}CH_2)$	Log	$\sigma_m^+(\beta)$	$D(R_\beta)^b$
c-Pr	Me	0.176	−0.754	−0.10	3.18
EtO	Me	0.180	−0.745	−0.10	3.18
MeO	Me	0.214	−0.670	−0.10	3.18
Me	Me	0.597[d]	−0.224	−0.10	3.18
Et	Et	0.900[d]	−0.046	−0.10	3.18
EtO	Ph	0.208×10^{-2}[c]	−2.682	0.11	4.90
Ph	Ph	0.475×10^{-3}[d]	−3.323	0.11	4.90
c-Pr	c-Pr	0.260×10^{-1}[d]	−1.585	−0.05	4.40[e]
EtO	EtO	0.135×10^{-2}[c,d]	−2.870	0.05[f]	5.17[f]
EtO	Br	0.206×10^{-2}[c]	−2.686	0.40	0.31
EtO	Cl	0.599×10^{-3}[c]	−3.223	0.40	1.80
MeO	MeO	0.146×10^{-2}[c,d]	−2.836	0.05	5.17
MeO	Et	0.281	−0.552	−0.10	3.18

[a] Average of cis and trans rates, from Table IV except as noted. The σ_m^+ value for Me is from E. Glyde and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1463 (1975); that for c-Pr is the average of the values from Y. E. Rhodes and L. Vargas, *J. Org. Chem.*, **38**, 4077 (1973). Others from H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958). [b] Double bond stabilization parameter (kcal/mol) from ref 8. [c] Derived from data in ref 15 and T. Okuyama and T. Fueno, *J. Polym. Sci., Part A-1*, **9**, 629 (1971), and T. Okuyama, T. Fueno, and J. Furukawa, *Bull. Chem. Soc. Jpn.*, **43**, 3256 (1970). [d] Rates statistically corrected. [e] Taken equal to *n*-alkyl plus 1.2 kcal/mol, see text. [f] Taken equal to MeO.

Table VI. Rates of Hydration of 1,2-Disubstituted Alkenes $R_\alpha CH{=}CHR_\beta$

No.	R_α	R_β	$\sigma_p^+ + 0.60(\sigma_m^+ + 0.08D - 0.084)$	k_2, $M^{-1}\,s^{-1}$	Log k_2
70	c-Pr[a]	Me	−0.43	0.271×10^{-4} (trans)	−4.57
71				0.624×10^{-4} (cis)	−4.21
74	EtO	Me	−0.68	0.159 (trans)	−0.80
75				0.476 (cis)	−0.32
76	Ph	Me	−0.14	0.112×10^{-6} (trans)	−6.95
77	MeO	Me	−0.74	0.0724 (trans)	−1.14
78				0.254 (cis)	−0.60
79	Me	Me	−0.27	0.176×10^{-7} (trans)[b]	−7.75
80				0.416×10^{-7} (cis)[b]	−7.38
81	Et	Et	−0.26	0.106×10^{-6} (trans)[b]	−6.97
82				0.890×10^{-7} (cis)[b]	−7.05
83	EtO	Ph	−0.47	0.261×10^{-2} (trans)[c]	−2.58
84				0.456×10^{-2} (cis)[c]	−2.34
72	c-Pr[a]	c-Pr	−0.34	0.370×10^{-5} (trans)[b]	−5.43
73				0.950×10^{-5} (cis)[b]	−5.02
85	EtO	EtO	−0.49	0.939×10^{-3} (trans)[b,c]	−3.03
86				0.370×10^{-2} (cis)[b,c]	−2.43
87	EtO	Br	−0.52	0.165×10^{-2} (trans)[b]	−2.78
88				0.545×10^{-2} (cis)[b]	−2.26
89	EtO	Cl	−0.44	0.504×10^{-3} (trans)[b]	−3.30
90				0.156×10^{-2} (cis)[b]	−2.81
91	MeO	MeO	−0.55	0.435×10^{-3} (trans)[b,c]	−3.36
92				0.175×10^{-2} (cis)[b,c]	−2.76
93	Ph	Ph	0.07	0.354×10^{-10} (trans)[b]	−10.45
94				0.318×10^{-9} (cis)[b]	−9.50
95	MeO	Et	−0.74	0.0948 (trans)	−1.02
96				0.333 (cis)	−0.48

[a] The value of σ_p^+ is revised from that used earlier, and is the average of two values derived from cumyl chloride solvolyses: −0.46 (R. C. Hahn, T. F. Corbin, and H. Schechter, *J. Am. Chem. Soc.*, **90**, 3404 (1968)); −0.48 (H. C. Brown and J. D. Cleveland, *J. Org. Chem.*, **41**, 1792 (1976)). [b] Observed rate divided by a statistical factor of 2. [c] Converted from rate in 80% dioxane by multiplication by the factor $k_2(H_2O)/k_2(80\%\ \text{dioxane})$ of 22.9. The factor was derived averaging the rate ratios in these solvents for EtOCH=CHMe (cis and trans), MeOCH=CHMe (cis and trans), and $MeOCH{=}CMe_2$. Rates in H_2O are from Table IV and for 80% dioxane from footnote *c*, Table V. The rate of $MeOCH{=}CMe_2$ in 80% dioxane was obtained by use of the $k(EtO)/k(MeO)$ factor (footnote *i*, Table IV).

In the discussion of these great rate differences four principal causes for the effects of substituents on the carbon undergoing protonation (the β carbon) may be considered: (1) electronic effects in the transition state; (2) stabilization of the ground state; (3) steric effects; and (4) the effect on rehybridization of the carbon undergoing protonation.

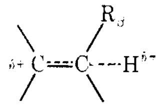
It may be seen in Table IV that there is a considerable variation in the effect on the rate of adding a β-methyl group, ranging from an increase of 1.7 to a decrease by a factor of 11. The magnitude of the effect is furthermore not related to the absolute reactivity of the alkene. This variation presumably arises from interactions between the vicinal substituents, and in the development of a simple theory we have not made a specific effort to account for this effect.

For the analysis of the β-substituent effects the rate ratios $k_{1,2\text{-disub}}/k_{\text{monosub}}$ are compiled in Table V together with appropriate substituent constants for the β substituents. For simplicity the average of the cis and trans rates are used. The comparisons chosen for initial consideration are between monosubstituted alkenes and 1,2-disubstituted alkenes in order to minimize steric effects, although the tri- and tetrasubstituted cases are discussed below.

Since the comparison of rates is made in terms of the $A_{SE}2$ mechanism, the rates for the symmetrically substituted alkenes **72, 73, 79–82, 85, 86,** and **91–94** have been divided by a statistical factor of 2 in Tables V and VI to account for the presence of two identical protonation sites in each of these molecules. This has the effect of reducing the spread in rate effects due to β-methyl groups to rate reductions in the range of 1.2–11, and also helps account for the fact that the observed rates of some 1,2-disubstituted alkenes are faster than those of their monosubstituted parents. Such a statistical factor was used previously in analysis of the rates of protonation of *cis*-stilbenes.[4]

It may be noted that those substituents that are inductively electron withdrawing, as measured by the σ parameters, have much larger rate retardations due to the β substituent. This trend is made apparent by plots of log $(k_{\mathrm{sub}}/k_{\mathrm{unsub}})$ vs. the parameters σ_m^+, σ_m, and σ_I, although the deviations from this approximate relation show that other factors are also involved. There is little to choose between the various substituent parameters for their ability to account for the data, so we have chosen σ_m^+ for the further discussion because of the not unreasonable analogy to our previous use of σ_p^+ for the α substituent.

The choice of σ_m^+ as the substituent parameter used may be justified in that the electronic interaction of the β substituent R in the transition state for protonation (5) is not unlike that



(5)

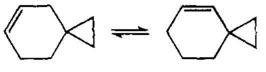
for a meta substituent in an electrophilic aromatic reaction.

The rate retardation in hydration due to the β-phenyl group in 2-methoxy-1-phenylpropene has been ascribed[5] to ground state stabilization of the alkene by the β-phenyl group. In Table IV the magnitude of the retardation is estimated at a factor of 135, which is comparable to the factors of 377–658 for retardation by the β-phenyl in 2-ethoxystyrene (Table V). The β-phenyl substituent also causes the largest of the deviations from the approximate correlation between rate retardation and σ_m^+, perhaps due to the ground state stabilization effect.

Quantitative estimates of the ability of substituents to stabilize double bonds have been derived by Hine and Flachskam.[8] Their D values, measured in kcal/mol, are included in Table V.

There is no value reported for the double bond stabilization parameter D for the cyclopropyl group. Calculation of the value as outlined by Hine and Flachskam[8] from the group additivity scheme for thermochemical properties[9] is also not applicable because the relevant parameters for cyclopropyl groups attached to double bonds are not listed. There are two heats of combustion reported[10,11] for vinylcyclopropane but the values do not agree and there is some doubt as to their reliability,[12] so it is probably unwise to use them as a basis for calculation.

The stabilization of a double bond by a cyclopropyl group has been estimated as 1.1–1.3 kcal/mol by Staley,[13] based on measurement of the equilibrium constant for the reaction shown in eq 6. Accordingly we have calculated a value of $D(\text{c-Pr}) = D(n\text{-alkyl}) + 1.2 = 4.4$ kcal/mol.


(6)

Combination of the transition state electronic term σ_m^+ and the ground state stabilization term D into a single relation gives

$$\log \frac{k_2(\mathrm{R}_\alpha\mathrm{CH{=}CHR}_\beta)}{k_2(\mathrm{R}_\alpha\mathrm{CH{=}CH_2})} = \rho'(\sigma_m^+ + bD) + c' \qquad (7)$$

and the optimum fit of the data is obtained where $\rho' = -7.4$, $b = 0.08$, and $c' = 0.62$, correlation coefficient 0.98 (Figure 1). Since the average rates for the cis and trans isomers were used the one case where only the trans rate was available was omitted. The deviations from this equation, evidenced by the scatter of the points and the nonzero intercept, may arise partly from other effects that were not considered, such as substituent–substituent interactions. Of the two terms in eq 7 that affect the rates the electronic destabilization of the charged transition state was dominant for β-halogen substituents, whereas ground state stabilization was more significant for the other groups.

Equation 8[1]

$$\log k_2(\mathrm{R}_\alpha\mathrm{CH{=}CH_2}) = \rho\sigma_p^+ + C \qquad (8)$$

correlates the rates of monosubstituted alkenes with $\rho = -12.3$ and $C = -10.1$. Combination of this equation with eq 7 gives

$$\log k_2(\mathrm{R}_\alpha\mathrm{CH{=}CHR}_\beta) = \rho[\sigma_p^+ + \rho'/\rho(\sigma_m^+ + bD + c'/\rho')] + C \qquad (9)$$

and on substitution of the numerical values of the constants this gives

$$\log k(\mathrm{R}_\alpha\mathrm{CH{=}CHR}_\beta) = -12.3[\sigma_p^+ + 0.60(\sigma_m^+ + 0.08D - 0.084)] - 10.1 \qquad (10)$$

The quantity in the brackets in eq 10 is listed for 27 compounds in Table VI. The form of eq 10 permits the data for these compounds to be plotted (Figure 2, squares) on the graph published earlier[1] for 1,1-disubstituted alkenes (circles) with approximately equal precision to the initial points. All 1,2-disubstituted alkenes that react by eq 4 for which the necessary data could be located in the literature are included in this correlation.

Previously an equation of the form

$$\log k = \rho(\sigma^+(\alpha) + a\sigma(\beta)) + C \qquad (11)$$

was used to correlate the rates of acid-catalyzed isomerization of 1,2-diarylethylenes where α and β refer to the substituents on the two aryl groups.[4] The success of this treatment indicates that variations in substituent effects on ground state stabilities either were minor in this series, or paralleled the effects on the transition states.

Equation 9 adequately represents the effect of β substituents on the rates of protonation by considering only the electronic effect on the transition state and the stabilization of the ground state. A variety of other factors must play a role, and the most obvious of these are discussed below. However, within the range of usefulness of the correlation it does not appear that their specific inclusion in eq 9 would result in an improvement in understanding.

The interaction between cis substituents, and the differences in cis and trans reactivities, are factors not included in eq 9. In all cases reported except the 2-butenes and the 3-hexenes the cis isomer is more reactive. This is not solely a reflection of a higher ground state energy of the cis isomer because in several cases the cis isomer has a lower ground state energy, for example, for **74/75** and **85/86**.[14] The steric factor is probably rather small, as evidenced by the fact that a β-*tert*-butyl substituent in ethyl vinyl ethers has a $k_{\mathrm{cis}}/k_{\mathrm{trans}}$ ratio of 7.1, barely twice that of the β-methyl substituent.[15c]

Specific interactions between cis substituents generally are destabilizing, but in some cases these factors are attractive, as evidently occurs in the cases in which the cis alkenes are more

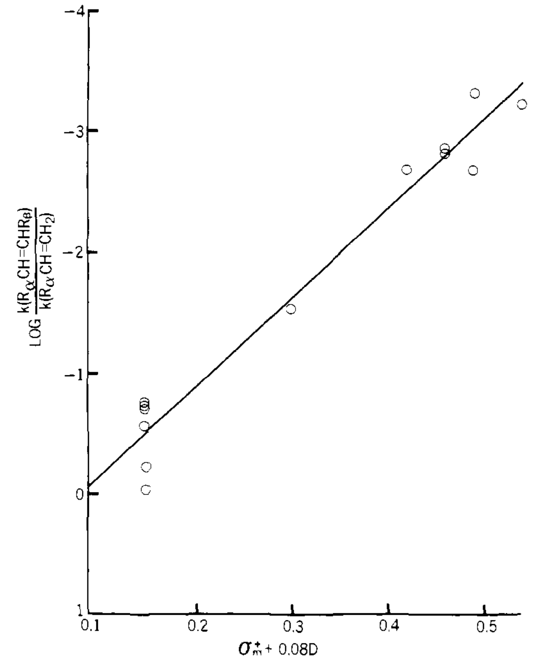


Figure 1. Correlation of the effects of β substituents on alkene hydrations.

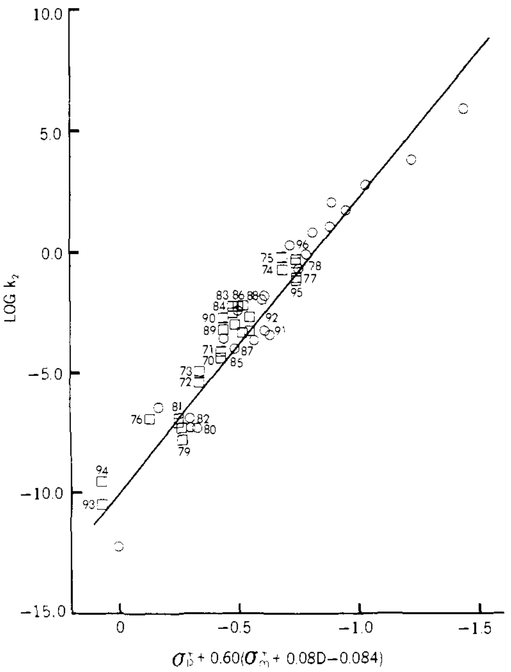


Figure 2. Hydration of 1,2-disubstituted alkenes (□).

stable than the trans. It has been suggested by Okuyama and Fueno[15a,b] that in the transition state for protonation a favorable Coulombic interaction occurs, and this effect may contribute to the generally observed greater reactivity of the cis alkenes. It would appear that detailed theoretical examination will be required to properly assess the role of this factor in hydrations.

In all cases but the comparison of 1-hexene to the 3-hexenes, and propene to *cis*-2-butene, the β substituent causes a retardation in the rate. For β-methyl groups the rate factor varies from 1.7 to 0.09, with most of the examples being rate retardations. Application of the statistical factor of 2 appropriate to the $A_{SE}2$ protonation of the symmetrical 3-hexenes and 2-butenes shows that in these cases the actual effect of the β-alkyl group is a small rate retardation. The fact that *trans*-cyclooctene and 2,3-dimethyl-2-butene show general acid catalysis[16] confirms that the $A_{SE}2$ mechanism is operative for symmetrically substituted aliphatic alkenes. The small rate decrease of 0.9 for 2,3-dimethyl-2-butene relative to isobutene shows that in this compound as well the favorable inductive effect of the β-methyls almost overcomes the adverse influences of these groups.

Two types of steric factors which would cause rate retardations by any β substituent are barriers to approach of the hydronium ion, and a barrier to rehybridization of a more heavily substituted carbon atom. These factors are not readily evaluated and have not been included. The correlation would not be significantly improved by including arbitrary corrections for them in any event.

The reactivity of the stilbenes deserves comment. According to eq 9 they are predicted to be less reactive than ethylene, but, as may be seen in Figure 2, they are about 100 times more reactive. However, the stilbenes fall much nearer the correlation line than does ethylene. The rate for ethylene was obtained by extrapolation[1] from measured rates at 170–190 °C to 25 °C, and may be subject to large errors. We intend to redetermine this very critical rate at room temperature.

Some of the tri- and tetrasubstituted alkenes show significant variations from the effect of the substituents in disubstituted alkenes. For example, the ratio $k((MeO)_2C{=}CH_2)/k((MeO)_2C{=}CMe_2)$ of 5.2×10^3 exceeds considerably that predicted from the product of the effect due to two trans substituents, or one cis and one trans substituent (ca. 10–100), and the ratio $k((EtO)_2C{=}CH_2)/k((EtO)_2C{=}CHCl)$ of 67 is less than the ratios of more than 10^3 for $k(EtOCH{=}CH_2)/k(EtOCH{=}CHCl)$. However, other such comparisons appear to be consistent with the disubstituted cases, namely, $k(MeOCMe{=}CH_2)/k(MeOCMe{=}CHPh) = 135$ whereas $k(EtOCH{=}CH_2)/k(EtOCH{=}CHPh) = 377$ and 658, and $k(MeOCH{=}CH_2)/k(MeOCH{=}CMe_2) = 30$ where the product of the cis and trans effects for $k(MeOCH{=}CH_2)/k(MeOCH{=}CHMe) = 33$. While it does not appear helpful to include the tri- and tetrasubstituted alkenes in the correlation, their deviations or agreement with the trends of the disubstituted alkenes serve to identify cases where additional interactions may occur.

In summary of the rate effects in 1,2-disubstituted alkenes the electronic effect of the β substituent on the developing carbonium ion (eq 5) appears to be a major effect of the substituent on reactivity, and the stabilization of the ground state by the substituent also plays an important role. A satisfactory correlation of the rates with those of 1,1-disubstituted alkenes may be obtained by considering these factors alone. There are other influences present including one that causes cis alkenes to be more reactive than trans. These include steric effects, specific substituent–substituent interactions, and substituent effects on rehybridizations. The effects in tri- and tetrasubstituted alkenes are greatly magnified in some cases and a general correlation of the reactivity of these compounds is not at present practical.

Experimental Section

Cyclopropylcarbinol and dicyclopropyl ketone were obtained from Aldrich Chemical Co. Cyclopropanecarboxaldehyde was prepared[17] from cyclopropylcarbinol by oxidation with ceric ammonium nitrate. Cyclopropylmethyl bromide, prepared from cyclopropylcarbinol and PBr_3,[18] was reacted with triphenylphosphine to give cyclopropylmethyltriphenylphosphonium bromide,[19] which was converted to the phosphorane[20] by treatment with *n*-butyllithium in ether. Wittig reaction of this phosphorane with cyclopropanecarboxaldehyde gave the 1,2-dicyclopropylethylenes **72** and **73**,[21] and reaction of cyclopropanecarboxaldehyde with ethylidenetriphenylphosphorane gave the 2-cyclopropylpropenes **70** and **71**.[21] The isomeric olefins were separated by gas chromatography[21] using a 1.5 m × 10 mm 40%

$AgNO_3$ on ethylene glycol column,[22] retention times **70**, 2.2 min at 50 °C; **71**, 6.6 min at 50 °C; **72**, 5.6 min at 65 °C; and **73**, 15.3 min at 65 °C. Tetracyclopropylethylene was prepared by thermolysis of the sodium salt of dicyclopropyl ketone *p*-tosylhydrazone.[21] The UV maxima of the cyclopropylalkenes, determined using a Cary 118 instrument swept with N_2, were in reasonable agreement with published values.[21,23]

Kinetics. The kinetics of the alkene hydrations were followed by monitoring the decrease in absorption of the alkenes in 1-cm cells using Cary 14 and 118 instruments. Acid solutions were prepared by dilution of concentrated reagent and concentrations were determined by titration with NaOH. Concentrated D_2SO_4 (Diaprep) was diluted with D_2O.

Injections of 10-μL aliquots of 0.02 M solutions of the alkenes in 95% ethanol into the sulfuric acid solutions in the UV cell gave final concentrations of 7×10^{-4} M alkene. The decrease of the absorption at the maxima was followed for at least 2 half-lives and good first-order kinetics were observed. At least three runs were carried out at each acid concentration. The absorption decreased by at least 80% in each case, indicating large equilibrium constants for hydration.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Research Council of Canada for support of this research.

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The Role of Tosylhydrazone Stereochemistry upon the Regiospecificity of Olefin Formation[1,2]

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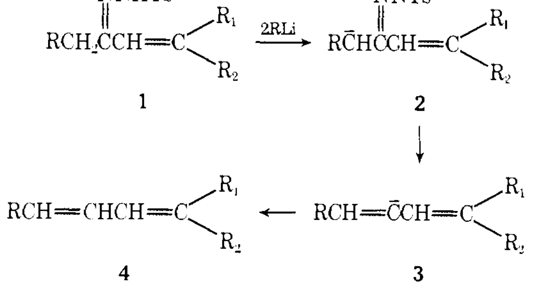
Received November 8, 1976

Abstract: The isomeric pulegone *p*-toluenesulfonylhydrazones (tosylhydrazones), **5**-*E* and **5**-*Z*, have been prepared and their structures have been established by x-ray crystallographic techniques. The alkyllithium mediated decomposition of these isomeric tosylhydrazones has been studied in order to evaluate the role of tosylhydrazone stereochemistry upon the regiospecificity of olefin formation. Significantly, decomposition of the isomeric tosylhydrazones in *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) leads to product where the tosylhydrazone stereochemistry seems to direct the course of the reaction while decomposition in benzene leads to the same product regardless of tosylhydrazone stereochemistry. The mechanism of this diene forming reaction has been established through the decomposition of a variety of α,β-unsaturated tosylhydrazones and through the synthesis and decomposition of specifically deuterated pulegone tosylhydrazones.

The alkyllithium mediated decomposition of *p*-toluenesulfonylhydrazones (hereafter called tosylhydrazones) of α,β-unsaturated ketones under mild conditions (0–20 °C) has been shown to yield conjugated 1,3-dienes in a regiospecific manner so that the position of the original carbon–carbon double bond in the unsaturated ketone is maintained in the diene.[3] Such dienes were postulated to be formed by α′-proton abstraction from the tosylhydrazone monoanion to yield the dianion **2** which subsequently decomposed to the vinyl anion **3** and this intermediate, in turn, was protonated to give the diene **4**. Recently, this reaction scheme has been established in the conversion of a ketone tosylhydrazone to an olefin.[4]



In the initial study[3] of enone tosylhydrazones, the derivative was prepared in tetrahydrofuran (trace of acid) and then this solvent was displaced by benzene prior to formation of the dianion with an ethereal solution of methyllithium. In some cases, it was found that the tosylhydrazone was thermally labile and the overall yield of the diene was decreased owing to difficulties encountered during the change in solvent or, in a few cases, during actual isolation of the derivative. To circumvent this problem, the procedure was modified and the entire reaction sequence from the unsaturated ketone to the 1,3-diene was conducted directly in tetrahydrofuran; in no case was the