Rates of Acid-Catalyzed Hydration of Isomeric *Z*/*E* Alkenes. Effects of Steric Crowding on Additions to Alkenes[†]

Willy K. Chwang and Thomas T. Tidwell*

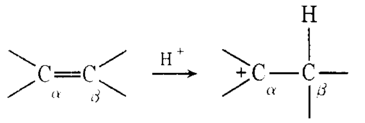
Department of Chemistry, University of Toronto, Scarborough College, West Hill, Ontario, Canada M1C 1A4

Received November 15, 1977

Rates of acid-catalyzed hydration of *Z*/*E* isomers of 2-butene, 3-hexene, 2,5-dimethyl-3-hexene, and 2,2,5,5-tetramethyl-3-hexene were measured at 25 °C in H_2O or 20% EtOH–80% aqueous H_2SO_4. The reactions proceeded by rate-determining protonation on carbon with rate ratios *Z*/*E* of 2.1, 1.2, 0.50, and 3.8, respectively. The results indicate little loss of steric strain in the transition state for protonation and are compared with the corresponding ratios in other electrophilic additions.

The reactivities of isomeric cis and trans olefins have been a topic of continuing interest in the study of electrophilic reactions.[1] In particular the relative reactivities of the isomeric 1,2-di-*tert*-butylethylenes have been used as a criterion of mechanism in the addition of *p*-chlorophenylsulfenyl chloride,[2a] mercuric acetate,[2b] bromine,[2c] and chlorine.[2d] These studies were intended to disclose whether bridged or open transition states occurred in these reactions. The reactivity of these isomers in catalytic hydrogenation was also used to study the mechanism of that process.[2e] However, rates of protonation, the prototype of an electrophilic reaction proceeding through an open transition state, have not been available for these compounds.

We have confirmed by a study of structural effects upon reactivities of alkenes in acid-catalyzed hydration reactions[3] that this reaction proceeds through $A_{SE}2$ rate-determining protonation on carbon (eq 1) and have established that the


(1)

effect of substituents on the reaction may be quantitatively correlated by eq 2 for 1,1-disubstituted alkenes.

$$\log k_2 = \rho\Sigma\sigma_p^+ + C \qquad (2)$$

When β substituents (eq 1) are also present the addition of terms to account for the effects of the β substituent on the ground-state stability of the alkenes and on the developing charge in the ion allows these compounds to be included in the correlation as well.

It appeared, therefore, highly desireable to utilize the mechanistic understanding gained of the hydration reaction for an analysis of the reactivity of geometrically isomeric alkenes, in particular the 1,2-di-*tert*-butylethylenes. We had previously collected the data available on the isomeric 2-butenes and 3-hexenes,[3d] but nothing had been reported on the higher homologues of this series.

Results

Hydration of the isomeric 2-butenes and 3-hexenes could be followed by observing the disappearance of the ultraviolet end absorption of the alkene chromophores in aqueous sulfuric acid as we have done previously.[3] However, the isomeric 1,2-diisopropyl- and 1,2-di-*tert*-butylethylenes were insufficiently soluble in this medium to utilize this method. Therefore rates were carried out in 20% ethanol–80% aqueous sulfuric acid, a medium for which the acidity function H_0 is available.[4] For comparison of the rates on a common basis the rates of the 3-hexenes were determined in each medium, and the relative reactivity factor for these substrates was used to calculate rates for all the substrates in aqueous sulfuric acid. The observed rates are collected in Tables I and II and are summarized in Table III with derived slopes and intercepts of log k vs. H_0 plots, solvent isotope effects, and *Z*/*E* rate ratios.

Our rates for (*Z*) and (*E*)-3-hexene in H_2SO_4 may be compared to data of Yates et al.[5a] in both cases and Modena et al.[5b] in the latter. Minor differences occur, with our rates being slightly greater in all cases, and the rates of Yates et al. being rather closer to ours than to those of Modena et al. The most significant differences are in the slopes of the log k vs. H_0 plots for the *E* isomer (-1.14[5b] as compared to our value of -1.35) and the fact that Yates et al. report $k(Z)/k(E) = 0.84$, whereas we find a value of 1.2. An objective assessment of the relative reliabilities of the sets of data does not appear practical, but our data are internally consistent, and in any event the differences between the different laboratories are minor.

The UV absorption decreased by at least 90% during the course of each of the reactions, indicating large equilibrium constants for hydration. However, in the case of the 1,2-diisopropyl and 1,2-di-*tert*-butylethylenes after about 5 half-lives for hydration a slow increase in the UV absorption became noticeable. In the case of the 1,2-di-*tert*-butylethylenes this eventually increased to a value greater than the absorption of the original alkenes. When 2,2,5,5-tetramethyl-3-hexanol (**1**), the expected product of direct hydration, was subjected to the reaction conditions the UV absorption increased with the approximate first-order rate constant of $3.2 \times 10^{-5}\ s^{-1}$ at 25 °C in 20% EtOH–80% H_2SO_4 containing 13.9 equiv $H^+\ kg^{-1}$. The same rate constant was observed for the slow increase in absorption beginning with either of the isomeric di-*tert*-butylethylenes.

Reaction of (*E*)-1,2-di-*tert*-butylethylene with a solution of 33% 14 M H_2SO_4 and 67% dioxane at 85 °C for 22 h led to a product mixture containing about 10% starting material and 90% 2,3,5,5-tetramethyl-2-hexene (**2**).[6] When the *Z* isomer was subjected to the same conditions the VPC trace of the product mixture showed the presence of about 5% starting material, 5% *E* isomer, and 90% **2**.

Repetition of the isomerization with *E* alkene in D_2SO_4 for 2 h led to the isolation of **2** whose NMR spectrum showed a sharp *t*-Bu peak but with considerably diminished and broadened signals for the vinyl methyl and CH_2 protons. The integrals of the last two peaks decreased by 80 and 72%, respectively, relative to the *tert*-butyl group. The mass spectrum of the undeuterated **2** showed the molecular ion at *m/e* 140 and strong signals at 125 ($M^+ - CH_3$), 83 ($M^+ -$ *t*-Bu), and 69 (perhaps $MeC^+HCH{=}CHMe$). The deuterated material showed strong signals at *m/e* 156–160, 149–151, 134–136, 93–95, and 76–78. This indicated the presence of two species, one containing 16–20 deuteriums and the other 9–11. As

---

[†] Dedicated to Professor M. S. Newman on the occasion of his 70th birthday.

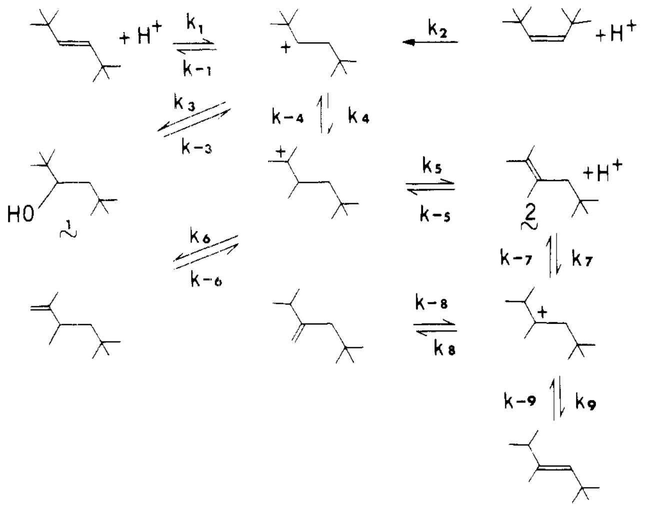
0022-3263/78/1943-1904$01.00/0

Table I. Rates of Hydration of Alkenes in Aqueous H_2SO_4 (25 °C)

Alkene	Registry no.	$[H_2SO_4]$(M)^a	H_0^{b}	k_{obsd}, s^{-1}
EtCH=CHEt^c (*Z*)	7642-09-3	8.63	−4.19	0.760×10^{-2}
		8.09	−3.91	0.269×10^{-2}
		7.47	−3.57	0.960×10^{-3}
		6.92	−3.28	0.407×10^{-3}
		8.82 (D_2SO_4)		0.972×10^{-2}
		6.93 (D_2SO_4)		0.350×10^{-3}
EtCH=CHEt^d (*E*)	13269-52-8	8.63	−4.19	0.594×10^{-2}
		8.09	−3.91	0.219×10^{-2}
		7.47	−3.57	0.792×10^{-3}
		6.92	−3.28	0.347×10^{-3}
		8.82 (D_2SO_4)		0.829×10^{-2}
		6.93 (D_2SO_4)		0.336×10^{-3}
MeCH=CHMe^e (*Z*) (2)	590-18-1	8.63	−4.19	0.793×10^{-2}
		8.09	−3.91	0.282×10^{-2}
		7.47	−3.57	0.928×10^{-3}
		6.92	−3.28	0.344×10^{-3}
		8.82 (D_2SO_4)		0.694×10^{-2}
MeCH=CHMe^f (*E*)	624-64-6	8.63	−4.19	0.354×10^{-2}
		8.09	−3.91	0.130×10^{-2}
		7.47	−3.57	0.456×10^{-3}
		6.92	−3.28	0.183×10^{-3}
		8.82 (D_2SO_4)		0.449×10^{-2}

[a] Measured by titration. [b] Interpolated from standard tables. [c] $\log k = -1.39H_0 - 7.96$ ($r = 0.999$). [d] $\log k = -1.35H_0 - 7.89$ ($r = 0.999$). [e] $\log k = -1.49H_0 -8.34$ ($r = 1.000$). [f] $\log k = -1.40H_0 - 8.35$ ($r = 0.999$).

Scheme I



outlined in the discussion this may be interpreted in terms of Scheme I.

The k_2 values calculated from extrapolation of the log k_{obsd} vs. H_0 plots to $H_0 = 0$ are somewhat less than those we derived earlier.[3d] As we have discussed before,[3e] this arises from the steep dependence of rate on acidity shown by these alkenes.

The solvent isotope effects (Table IV) are compared at equal molarities. As we have noted before,[3e] this is reasonable inasmuch as the acidity functions of H_2SO_4 and D_2SO_4 are essentially identical at the same molarity except in very dilute acids and above 97% acid.

Discussion

The dependence of the rates on acidity and the reactivities of the alkenes are consistent with the reactions proceeding by rate-determining protonation on carbon to give carbonium ions (the $A_{SE}2$ mechanism, eq 1). This is supported by the results obtained on a wide variety of other alkenes of diverse structural types.[3] As we have noted elsewhere[3e] solvent isotope effects vary within a considerable range for alkene protonations and are not an unambiguous criterion of mechanism. The values found here are within the limits reported for others reacting by the $A_{SE}2$ route.

The initial decrease in absorption in each case suggests that following the rate-determining steps the resulting carbonium ions then undergo hydration to the corresponding carbinols. This is in accord with the generally observed 1,2 additions of a variety of electrophiles which has been noted for these compounds. For example, HBr-catalyzed addition of acetic acid to the 2-butenes and 3-hexenes,[7] trifluoroacetic acid addition to the 3-hexenes,[8] bromination of the 1,2-diisopropylethylenes,[2c] and chlorination[2d] of the 1,2-di-*tert*-butylethylenes occur predominantly by this route.

The initial sharp drop in the ultraviolet absorption during reaction of the 1,2-di-*tert*-butylethylenes implies that the hydration product **1** is initially formed, although this material was not actually isolated. The slower formation of a substance with a stronger UV absorption at the same rate from either *E* or *Z* alkene, or authentic **1**, and the isolation of **2** strongly supports this pathway, as shown in Scheme I.

The possibility must be considered that the (*Z*)-di-*tert*-butyl alkene is being rapidly converted to the *E* isomer so that the observed rate of reaction of the *Z* isomer corresponds to consumption of the *E* isomer. However, that $k(Z)/k(E)$ for the 1,2-di-*tert*-butylethylene has a close correspondence to k_2/k_1 (Scheme I) is supported by several lines of evidence. The fact that $k(Z)$ exceeds $k(E)$ by a factor of 3.8 (Table III) shows that isomerization of *Z* to *E* is not extensive, as this process if complete would result in identical observed rate constants beginning with either isomer. The presence of some residual *Z* isomer after 90% conversion to **2** also indicates that the conversion of *Z* to *E* is not a major route, and the fact that when the *E* isomer is converted to **2** to the extent of 25% in D_2SO_4 the recovered *E* isomer contains only 2% deuterium indicates that $k_4 > k_{-1}$ (Scheme I).

The deuterium distribution of **2** formed in D_2SO_4 is highly revealing as to the course of the reaction. Much of **2** contains 9–11 atoms *D*, but the NMR spectrum of the product shows a sharp *tert*-butyl signal, indicating that none of **2** with a partially deuterated *tert*-butyl group is present. The absence of mass spectral peaks corresponding to the incorporation of

Table II. Rates of Reaction of Alkenes in 20% EtOH–80% H_2SO_4 (25 °C)

Alkene	Registry no.	Equiv H^+, kg^{-1}[a]	H_0	k_{obsd}, s^{-1}
t-BuCH=CH-*t*-Bu (*Z*)[b]	692-47-7	11.3	−4.51	1.61×10^{-2}
		10.6	−3.95	2.67×10^{-3}
		10.0	−3.62	1.14×10^{-3}
		9.65	−3.39	4.92×10^{-4}
		10.9 (D_2SO_4)		4.31×10^{-3}
t-BuCH=CH-*t*-Bu (*E*)[c]	692-48-8	12.0	−5.07	1.93×10^{-2}
		11.3	−4.51	4.86×10^{-3}
		10.6	−3.95	6.61×10^{-4}
		10.0	−3.62	2.82×10^{-4}
		10.9 (D_2SO_4)		1.46×10^{-3}
		10.7 (D_2SO_4)		1.06×10^{-3}
i-PrCH=CH-*i*-Pr (*Z*)[d]	10557-44-5	11.3	−4.51	2.29×10^{-3}
		10.6	−3.95	4.61×10^{-4}
		10.3	−3.62	2.26×10^{-4}
		9.65	−3.39	1.19×10^{-4}
		10.9 (D_2SO_4)		1.16×10^{-3}
		10.2 (D_2SO_4)		2.94×10^{-4}
i-PrCH=CH-*i*-Pr (*E*)[e]	692-70-6	11.3	−4.51	5.64×10^{-3}
		10.6	−3.95	8.37×10^{-4}
		10.0	−3.62	4.96×10^{-4}
		9.65	−3.39	2.14×10^{-4}
		10.9 (D_2SO_4)		2.47×10^{-3}
		10.7 (D_2SO_4)		1.44×10^{-3}
EtCH=CHEt (*Z*)[f]		11.3	−4.51	1.23×10^{-2}
		10.6	−3.95	2.07×10^{-3}
		9.65	−3.39	7.11×10^{-4}
		9.08	−3.05	2.43×10^{-4}
		10.9 (D_2SO_4)		4.26×10^{-3}
		10.7 (D_2SO_4)		2.82×10^{-3}
EtCH=CHEt (*E*)[g]		11.3	−4.51	1.05×10^{-2}
		10.6	−3.95	1.94×10^{-3}
		9.65	−3.39	5.31×10^{-4}
		9.08	−3.05	2.06×10^{-4}
		10.9 (D_2SO_4)		4.15×10^{-3}
		10.7 (D_2SO_4)		2.51×10^{-3}

[a] Determined by titration. [b] $\log k = -1.33H_0 - 7.80$ ($r = 0.999$). [c] $\log k = -1.30H_0 - 8.26$ ($r = 0.997$). [d] $\log k = -1.13H_0 - 7.78$ ($r = 0.999$). [e] $\log k = -1.23H_0 - 7.83$ ($r = 0.992$). [f] $\log k = -1.13H_0 - 7.04$ ($r = 0.995$). [g] $\log k = -1.15H_0 - 7.20$ ($r = 0.999$).

Table III. Comparative Rates and Isotope Effects of Protonation of Alkenes RCH=CHR

	k_{H^+}/k_{D^+}[a]		k_2[b]	
R	*Z*	*E*	*Z*	*E*
Me	1.56	1.04	4.53×10^{-9}	4.48×10^{-9}
Et	1.14	1.06	1.10×10^{-8}	1.27×10^{-8}
i-Pr	0.92	0.96	2.77×10^{-9}	6.82×10^{-9}
t-Bu	1.47	1.05	1.95×10^{-8}	5.88×10^{-9}

[a] Average of all values in aqueous H_2SO_4 and in 20% EtOH–80% aqueous H_2SO_4 solutions calculated as k_{obsd} [HA]/k_{obsd} [DA] at the molarities of DA reported in Tables I and II using rates of HA interpolated to the same molarity. [b] $k_2 = k_{obsd}/h_0$ at $h_0 = 1$; rates not statistically corrected. For R = *i*-Pr and *t*-Bu rates are for aqueous H_2SO_4 solution estimated from the observed rates in 20% EtOH–80% H_2SO_4 by multiplying the rate ratio of the alkene to (*E*)-3-hexene at 11.3 equiv H^+ kg^{-1} in 20% EtOH by the k_2 value of (*E*)-3-hexene. At $H_0 = 0$ the average of the rates in H_2O–H_2SO_4 of the (*E*)- and (*Z*)-3-hexenes is 0.16 times the rates in 20% EtOH.

12–15 deuteriums is in accord with this conclusion. This result could occur by conversion of the initial *secondary* ion to a *tertiary* ion via k_4 and then rapid interconversion of *tertiary* ions via k_5–k_9 and their reversal. Some of **2** contained 16–19 atoms *D* and was thus approaching complete deuteration. This could occur by an occasional reformation of the *secondary* ion from the *tertiary* ion via k_{-4} followed by either deprotonation (k_{-1}) or hydride migration to give the isomeric *secondary* ion with the same carbon skeleton. Rapid conversion to a *tertiary* ion and complete equilibration of the hydrogens would then follow.

The rates of reaction suggest that several competing structural factors on reactivity are operative. The 3-hexenes tend to be more reactive than the 2-butenes, suggesting a greater electron donation by the ethyl groups relative to methyl. (*Z*)-1,2-Diisopropylethylene is distinctly the least reactive of the group, giving rise to the only $k(Z)/k(E)$ ratio less than 1.0. (*Z*)-1,2-Di-*tert*-butylethylene is the most reactive of the group, suggesting some relief in the transition state of the 10 kcal/mol steric strain[9] present in the ground state of this molecule. For RCH=CHOEt the *t*-Bu/Me rate ratio is 1.2 for the *Z* isomers and 0.6 for the *E* isomers, and the *Z*/*E* ratios are 7.1, 5.7, 3.8, and 3.2 for R = *t*-Bu, *i*-Pr, Et, and Me, respectively.[10a] Steric hindrance to solvation in the developing cation might have been expected to be a significant factor, as the solvation energy from interaction of solvent with the π cloud in (*E*)-1,2-di-*tert*-butylethylene has been found to be negligible for DMF solvent.[10b,c] However, in MeOH solvent steric hindrance does not appear to reduce the solvation energy.[10b,c] In the present case the change in solvation energy between the ground state and transition states is the significant quantity, and no major change between the different pairs is noticeable.

Correlation of the rates by the extended version of eq 2 used for 1,2-disubstituted alkenes[3d] is straightforward and these substrates fit the correlation within the limits previously established. Even for these crowded substrates an explicit term to account for ground state strain is unnecessary.

The most surprising feature of this work is the low $k(Z)/$

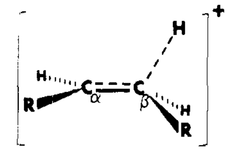
Table IV. Relative Reactivities ($k(Z)/k(E)$) of Isomeric Alkenes toward Various Electrophiles

	Electrophile				
Alkene	H_3O^+[a]	ArSCl[b]	$Hg(OAc)_2$	Br_2	Cl_2
t-BuCH=CH-t-Bu	3.8	1.58 × 10^5	>100[d]	51.9[e]	0.37[c]
i-PrCH=CH-i-Pr	0.50	9.7		0.42[e]	
EtCH=CHEt	1.2	9.2	6.2[f]	1.1[e,h]	
MeCH=CHMe	2.1	3.1	3.4[g]	1.3[e,h]	1.3[i]

[a] This work. [b] G. H. Schmid, C. L. Dean, and D. G. Garratt, *Can. J. Chem.*, **54,** 1253 (1976). [c] Reference 2d. [d] Reference 2b, and R. D. Bach and R. F. Richter, *Tetrahedron Lett.*, 4099 (1973). [e] K. Yates and R. S. McDonald, *J. Org. Chem.*, **38,** 2465 (1973), and ref 2c. [f] H. J. Bergman, G. Collin, G. Just, G. Müller-Hagen, and W. Pritzkow, *J. Prakt. Chem.*, **314,** 285 (1972). [g] J. Halpern and H. B. Tinker, *J. Am. Chem. Soc.*, **89,** 6427 (1967). [h] G. A. Olah and T. R. Hockswender, Jr., *J. Am. Chem. Soc.*, **96,** 3574 (1974); see also J. E. Dubois and G. Mouvier, *Bull. Soc. Chim. Fr.*, 1426 (1968). [i] M. L. Poutsma, *J. Am. Chem. Soc.*, **87,** 4285 (1965).

$k(E)$ ratio of only 3.8 for the 1,2-di-*tert*-butylethylenes. This ratio is much less than those observed for arylsulfenyl halide addition, bromination, or oxymercuration (Table IV) (reactions that we have concluded proceed through bridged intermediates for these but not all substrates).[11] It might well have been anticipated that protonation of the 1,2-di-*tert*-butylethylenes would have led to an even greater $k(Z)/k(E)$ ratio than for the reactions leading to bridged transition states. Thus formation of an open ion (Scheme I) might allow relief of a great deal of the 10 kcal/mol strain present in the Z isomer, particularly since alkene hydrations are proposed to have late transition states.[12]

The transition state model[13] below for this reaction may help to explain this result. During protonation there is probably little twisting around the central C–C bond as there is still significant double bond character remaining. The R group on C_β is depressed from the plane of the groups on C_α, but at the same time the decreasing C_α–C_β–R angle tends to minimize any movement of the R groups away from one another in the transition state. Only in the fully formed intermediate can significant rotation around the central C–C bond occur with concomitant reduction of the R–R repulsion.



As for the reactions involving bridged transition states we have suggested that steric approach control is the decisive rate-determining factor.[2a] Thus in the E isomer both sides of the molecule are blocked to attack of the electrophile, whereas in the Z isomer one side of the molecule is unhindered. This factor appears to be much less important in protonations, possibly due to a combination of lower steric requirement for the electrophile and because of a more open direction of approach.

Experimental Section

(E)- and (Z)-2-Butene were obtained from Matheson Gas Products and the isomeric 3-hexenes and 2,5-dimethyl-3-hexenes and (E)-2,2,5,5-tetramethyl-3-hexene were obtained from Chemical Samples Co. (Z)-2,2,5,5-Tetramethyl-3-hexene was obtained by hydrogenation of 2,2,5,5-tetramethyl-3-hexyne over Raney nickel.[9] Deuterated acids and solvents were obtained from Aldrich-Diaprep.

Kinetics were performed by injecting 10-μL samples of 0.3 M solutions of the alkenes in MeOH into 3 mL of the acid solution in 1-cm cells thermostated at 25 °C in a Cary 118 spectrophotometer and monitoring the decrease in absorbance at 197.5 nm. Solutions of 20% EtOH–80% H_2SO_4 were prepared as described.[4] Deuterated solutions were prepared by dilution of D_2SO_4 with D_2O or EtOD. Acid concentrations were measured by titration with standard NaOH and were converted to weight percentages using standard tables.[3,4] At least two runs were made at each acidity.

The product study of (E)-2,2,5,5-tetramethyl-3-hexene was carried out by heating 0.35 g (2.5 mmol) of the alkene in a mixture of 10 mL of dioxane and 5 mL of 14 M H_2SO_4 in a sealed ampule at 85 °C for 22 h. The mixture was then extracted with ether, washed with NaCl and $NaHCO_3$ solutions, and dried over Na_2CO_3. After evaporation of volatile solvent the residue was analyzed by gas chromatography using a 3 M × 10 mM 20% FFAP column at 120 °C and 60 mL/min He. The major product, retention time 15 min, showed a mass spectrum (70 eV) with peaks (rel heights) at m/e 140 (M^+, 10), 125 ($M^+ - CH_3$, 43), 97 (16), 84 (23), 83 (M^+ − t-Bu, 68), 82 (12), 71 (11), 70 (72), 69 (100), 37 (t-Bu^+, 40), and 55 (40) and NMR (CCl_4) δ 0.88 (s, 9, t-Bu), 1.68 (s, 9, 3 vinyl Me), and 2.00 (s, 2, CH_2-t-Bu) and was identified as 2,3,5,5-tetramethyl-2-hexene (**2**) by comparison of the NMR with that of an authentic sample.[6] Approximately 10% of the starting material was still present.

Treatment of the Z isomer under the same conditions led to a product mixture consisting of 90% of **2** and peaks in the gas chromatogram corresponding to 5% each of the (Z)- and (E)-2,2,5,5-tetramethyl-3-hexenes. Comparable results were obtained with either isomer when the dioxane was absent from the reactant mixture.

The E alkene (0.35 g, 2.5 mmol) was also heated with a mixture of 4 mL of 18 M D_2SO_4, 1 mL of D_2O, and 10 mL of dioxane for 2 h at 85 °C. After extraction the mixture was separated by gas chromatography as above and found to consist of about 75% starting material and 25% of the material with the same retention time as **2**. The mass spectrum (70 eV) of the former indicated the incorporation of 2% deuterium. The NMR of the latter corresponded to that of **2**, but the vinyl methyl and methylene absorptions had broadened and diminished in area by 80 and 72%, respectively, in their areas relative to the t-Bu peak in the undeuterated material. The mass spectrum (70 eV) showed peaks (rel heights) at m/e 160 (2), 159 (3), 158 (4), 157 (3), 156 (1), 151 (7), 150 (8), 149 (5), 148 (2), 136 (3), 135 (5), 134 (3), 96 (13), 95 (43), 94 (57), 93 (38), 92 (20), 91 (10), 78 (14), 77 (23), 76 (18), 75 (11), 74 (8), 66 (19), 65 (18), 62 (18), 61 (15), and 57 (100).

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.

References and Notes

(1) For general reviews, see: (a) R. Bolton in "Comprehensive Chemical Kinetics", Vol. 9, C. H. Bamford and C. F. H. Tipper, Ed., Elsevier, New York, N.Y., 1973; (b) P. D. B. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems", Elsevier, Amsterdam, 1966; (c) G. H. Schmid and D. G. Garratt in "Chemistry of the Alkenes", Vol. 2, Supplement A, J. Zabicky, Ed., Wiley-Interscience, New York, N.Y., 1977; (d) T. Okuyama and T. Fueno, *Kagaku No Ryoiki*, **29,** 17 (1975).

(2) (a) C. L. Dean, D. G. Garratt, T. T. Tidwell, and G. H. Schmid, *J. Am. Chem. Soc.*, **96,** 4958 (1974); (b) R. D. Bach and R. F. Richter, *J. Org. Chem.*, **38,** 3442 (1973); (c) K. Yates and R. S. McDonald, *J. Am. Chem. Soc.*, **93,** 6297 (1971); (d) R. Fahey, *ibid.*, **88,** 4681 (1966); (e) H. H. Kung, R. J. Pellet, and R. L. Burwell, Jr., *ibid.*, **98,** 5603 (1976).

(3) Literature data are summarized in the references below, especially the last: (a) K. Oyama and T. T. Tidwell, *J. Am. Chem. Soc.*, **98,** 947 (1976); (b) W. K. Chwang, P. Knittel, K. M. Koshy, and T. T. Tidwell, *ibid.*, **99,** 3395 (1977); (c) S. Y. Attia, J. P. Berry, K. M. Koshy, Y.-K. Leung, E. P. Lyznicki, Jr., V. J. Nowlan, K. Oyama, and T. T. Tidwell, *ibid.*, **99,** 3401 (1977); (d) P. Knittel and T. T. Tidwell, *ibid.*, **99,** 3408 (1977); (e) W. K. Chwang, V. J. Nowlan, and T. T. Tidwell, *ibid.*, **99,** 7233 (1977); (f) V. J. Nowlan and T. T. Tidwell, *Acc. Chem. Res.*, **10,** 252 (1977).

(4) A. J. Kresge, and H. J. Chen, *J. Am. Chem. Soc.*, **94,** 8192 (1972).

(5) (a) K. Yates, G. H. Schmid, T. W. Regulski, D. G. Garratt, H.-W. Leung, and R. McDonald, *J. Am. Chem. Soc.*, **95,** 160 (1973); (b) G. Modena, F. Rivetti, G. Scorrano, and U. Tonellato, *ibid.*, **99,** 3392 (1977).

(6) J. E. Dubois, J. S. Lomas, and D. S. Sagatys, *Tetrahedron Lett.*, 1349 (1971); the identification of **2** was kindly confirmed by Dr. Lomas by a comparison of NMR spectra.

(7) D. J. Pasto, G. R. Meyer, and B. Lepeska, *J. Am. Chem. Soc.*, **96,** 1858 (1974).

(8) P. E. Peterson and G. Allen, *J. Org. Chem.*, **27,** 1505 (1962).

(9) R. B. Turner, D. E. Nettleton, Jr., and M. Perelman, *J. Am. Chem. Soc.*, **80,** 1430 (1958); W. H. Puterbaugh and M. S. Newman, *ibid.*, **81,** 1611 (1959).

(10) (a) T. Okuyama, T. Fueno, H. Nakatsuji, and J. Furukawa, *J. Am. Chem. Soc.*, **89,** 5826 (1967); (b) P. P. S. Saluja, T. M. Young, R. F. Rodewald, F. H.

Fuchs, D. Kohli, and R. Fuchs, *ibid.*, **99**, 2949 (1977); R. Fuchs and P. P. S. Saluja, *Can. J. Chem.*, **54**, 3857 (1976).

(11) (a) T. R. Cerksus, V. M. Csizmadia, G. H. Schmid, and T. T. Tidwell, *Can. J. Chem.*, **56**, 205 (1978); (b) G. H. Schmid and T. T. Tidwell, *J. Org. Chem.*, **43**, 460 (1978); (c) I. C. Ambidge, S. K. Dwight, C. Rynard, and T. T. Tidwell, *Can. J. Chem.*, **55**, 3086 (1977).

(12) Y. Chiang, A. J. Kresge, and J. R. Wiseman, *J. Am. Chem. Soc.*, **98**, 1564 (1976).

(13) For a summary of theoretical treatments of the alkene protonation transition state see ref 3e and 3f.

Reaction of Singlet Oxygen with 2-Methylnorbornadiene and 2-Methylidenenorbornene. Evaluation of Electronic and Steric Effects on the Course of Hydroperoxidation

Charles W. Jefford* and Christian G. Rimbault

Département de Chimie Organique, Université de Genève 30, 1211 Genève 4, Switzerland

Received August 30, 1977

The dye-sensitized photooxygenation of 2-methylnorborna-2,5-diene (**5**) and 2-methylidenenorborn-5-ene (**6**) has been studied. Olefin **5** gave the expected allylically rearranged exo and endo hydroperoxides in a ratio of 7.3:1. Olefin **6** gave the allylically rearranged hydroperoxide (98%) together with the exo and endo epoxides deriving from the methylidene function (2%). The rates of photooxygenation of **5** and **6** were compared with those obtained with 2-methylnorborn-2-ene (**1**), 2-methylidenenorbornane (**2**), 1-methylcyclopentene (**7**), and methylidenecyclopentane (**8**). The partial rates for oxygen attack on the exo faces of the bicyclic olefins were found to parallel the ionization potentials of the reacting double bonds. An interpretation of electronic and steric effects was made in terms of the formation of an activated complex arising from the interaction of the HOMO of the olefin with the LUMO of singlet oxygen.

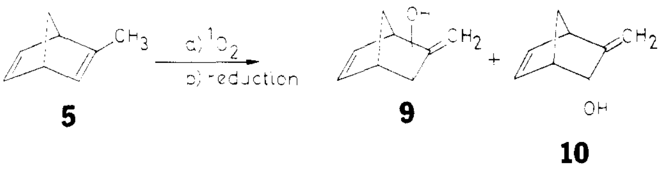
Norbornene is a substrate par excellence for the study of the mechanism of reactions occurring at the double bond. Norbornene itself is slowly oxidized by singlet oxygen, but cannot give hydroperoxide in an ene-type reaction as the allylic carbon–hydrogen bond lies in the nodal plan of the double bond.[1] However, 2-methylnorbornene (**1**) and 2-methylidenenorbornane (**2**) react readily to give the allylic hydroperoxides.[2]

Compounds **1** and **2**, unlike simple olefins, only undergo the "ene" reaction in one direction. Furthermore, the approach of the oxygen molecule is differentiated by the exo and endo faces of the norbornyl skeleton. By studying rates of photooxygenation and product analyses of **1** and **2** together with their 7,7-dimethyl derivatives **3** and **4** (Table I) we discovered that, while the endo sides in the series **1–4** are really indistinguishable, the partial rates for the exo side varied significantly.[3]

The presence of methyl at C(7) depressed the rate of attack by oxygen much more at an internal than an external double bond. We concluded that steric hindrance in the ground-state structures is an important rate-determining factor for the hydroperoxidation reaction. We deduced that steric strictures operate in the formation of the carbon–oxygen bond, but not in the abstraction of the allylic hydrogen atom, and further that the former event precedes the latter. As a consequence the transition state should have dipolar character; partial negative charge would accumulate on the terminal oxygen atom counterbalancing positive charge dispersed hyperconjugatively over the allylic portion (Figure 1). There are two important corollaries, if this picture is correct. The first is that when steric and statistical differences are negligible for a pair of competing "ene" modes, then the products should be partitioned according to the relative importance of the Markownikoff effects. The second is that, as oxygen behaves as an electrophile, rates ought to be determined by the relative energies of the respective frontier orbitals.

In this paper we examine the validity of this second corollary by modifying the molecular orbital levels of the reacting olefin by introducing a second double bond, but which is essentially inert to singlet oxygen. The substrates chosen are 2-methylnorbornadiene (**5**) and 2-methylidenenorbornene (**6**). The kinetics and stereochemistry of the photooxygenation of **5** and **6** are compared with the monoolefinic parents **1** and **2** together with the monocyclic olefins, 2-methylcyclopentene (**7**) and 2-methylidenecyclopentane (**8**).

Scheme I

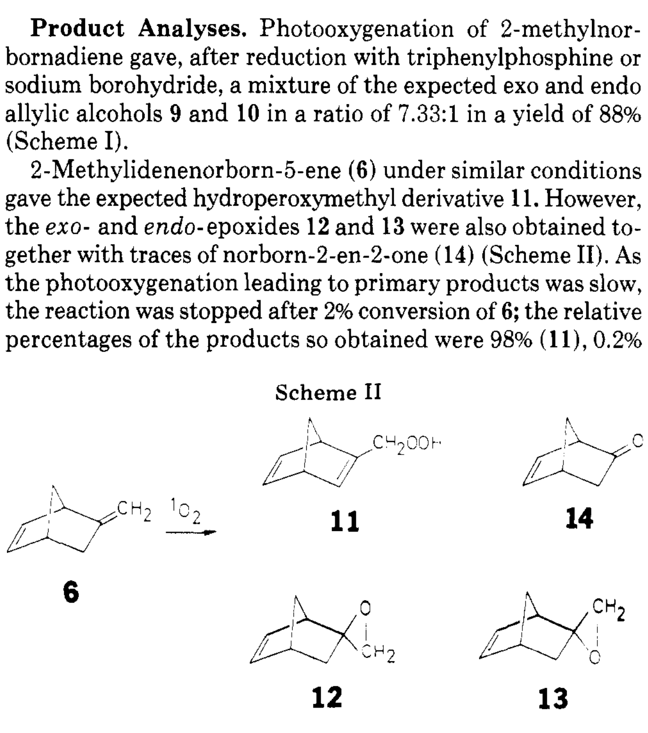


Results

Product Analyses. Photooxygenation of 2-methylnorbornadiene gave, after reduction with triphenylphosphine or sodium borohydride, a mixture of the expected exo and endo allylic alcohols **9** and **10** in a ratio of 7.33:1 in a yield of 88% (Scheme I).

2-Methylidenenorborn-5-ene (**6**) under similar conditions gave the expected hydroperoxymethyl derivative **11**. However, the *exo*- and *endo*-epoxides **12** and **13** were also obtained together with traces of norborn-2-en-2-one (**14**) (Scheme II). As the photooxygenation leading to primary products was slow, the reaction was stopped after 2% conversion of **6**; the relative percentages of the products so obtained were 98% (**11**), 0.2%

Scheme II



0022-3263/78/1943-1908$01.00/0