Cyclopropyl Substituent Effects on Acid-Catalyzed Hydration of Alkenes. Correlation by σ^+ Parameters[1]

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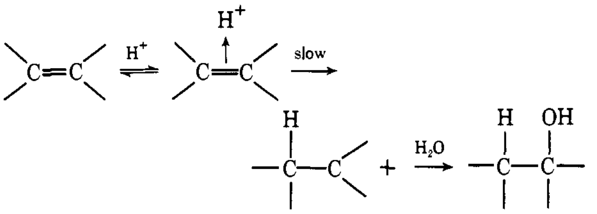
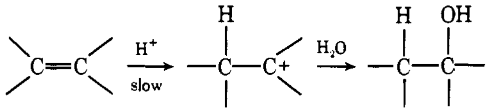
Abstract: Rate constants of acid-catalyzed hydration of cyclopropylalkenes c-PrCR$=$CH$_2$ at 25° in H$_2$O and D$_2$O were determined for R = H, Me, Ph, and c-Pr. The initial products were the alcohols c-PrCOHRCH$_3$, but rearrangement then occurred for R = c-Pr to 2-cyclopropyl-2-methyltetrahydrofuran, and for R = Ph to (Z)-2-phenylpent-2-en-5-ol. The data indicate the reactions proceed through rate-determining protonation of the double bond. The log k values for these reactions and others in the literature correlate with Brown σ^+ parameters over a range of 10^{18} in reactivity, with $\rho^+ = -12$.

The elucidation of the mechanism of the acid-catalyzed hydration of alkenes has been the goal of many chemical investigations.[2,3] It was originally proposed by Taft that these reactions involved reversible formation of a π complex which rearranged in a slow step to a carbonium ion (eq 1).[4]



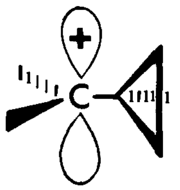
(1)

However, there is now a considerable body of evidence that many systems proceed via the A-SE2 mechanism of rate-limiting protonation of the double bond (eq 2). This evidence includes the correlation of the reactivities of styrenes with σ^+ constants for substituents on the aromatic ring,[5a] the rate dependence on acidity function,[5b] solvent isotope effects,[5a] and the observation of general acid catalysis in some cases.[2a,5a] The acid-catalyzed methanolysis of 1,1-bis(p-dimethylaminophenyl)ethylene proceeds by the A-SE2 route and has been completely analyzed in terms of the rate constants connecting reactant, intermediate ion, and product.[6] An exceptional case which does not proceed by the A-SE2 route is 9-methoxyoxacyclonon-2-ene,[2b] which apparently undergoes reversible protonation of the double bond followed by a slow subsequent step.



(2)

We have recently established that the substituent effect of the cyclopropyl group on the rate of electrophilic additions to alkenes is a powerful tool for the examination of transition state structures.[1a] This group has the unique property of being a strong electron donor by resonance while being weakly electron withdrawing inductively.[7] The conjugative donation of the group is furthermore only effective when a bisected conformation can be achieved with the plane of the cyclopropyl group parallel with the p orbital of the carbonium ion center.[8]



There have been several attempts at the correlation of the reactivities of selected groups of alkenes with substituent effects. For example, the reactivities of alkenes substituted with methyl, phenyl, and acetoxy groups toward protonation have been discussed in terms of their rate ratios, especially as compared to solvolytic reactions.[9] The rates of hydration of aryl-substituted styrenes have been successfully correlated by the extended Hammett equation of Brown using the electrophilic substituent parameters σ^+.[5a] Application of the multiparameter Taft equation

$$\log k/k_0 = \alpha\sigma_\mathrm{I} + \beta\sigma_\mathrm{R} + h$$

to hydration data for a group of seven alkenes with substituents attached directly to the double bond gave a fit described as "very good" with a multiple correlation coefficient of 0.96.[10a] The Taft equation has also been applied to other electrophilic additions.[10] The rate of hydration of para-substituted α-methoxystyrenes gave a curved correlation with the σ^+ constants, but the multiparameter Yukawa-Tsuno equation (3) gave an improved fit of the data.[11]

$$\log k/k_0 = \rho[\sigma + r(\sigma^+ - \sigma)] \tag{3}$$

It appeared desirable therefore to attempt a more general correlation of substituent effects on alkene hydrations. Accordingly, we have examined the reactivity of substituted cyclopropylalkenes and have obtained a highly satisfactory correlation of these results together with data in the literature with Brown's electrophilic substituent parameter σ^+.

Results

The rates of acid-catalyzed hydrolysis of vinylcyclopropane (**1**), 1-methyl-1-cyclopropylethylene (**2**), 1-phenyl-1-cyclopropylethylene (**3**), and 1,1-dicyclopropylethylene (**4**) in water at 25° were measured by observing the decrease in ultraviolet absorption of the alkene chromophores. The aliphatic alkenes gave stable end points after 10 half-lives, but **3** displayed increasing absorption on standing. This behavior apparently arises because the product rearranges to another product containing a styrene chromophore, as noted below. All the alkenes gave excellent pseudo-first-order rate plots. Rate constants obtained for normal and deuterated solutions and different acid strengths are given in Table I, along with the calculated solvent isotope effects. Data were also assembled for an additional 19 alkenes (**5**–**23**) studied by others.

For comparisons at constant acidities, rates for α-methylstyrene (**21**) and styrene (**22**) were also measured and are included in Table I. Rates of hydration of the alkenes **1**–**4** and **21** relative to styrene were calculated, wherever possible using comparisons of observed rate constants at common acidities as noted in Table I. Small variations in the rate ratios are observed at different acidities.

Table I. Rates of Acid-Catalyzed Hydration of Alkenes $R_1R_2C{=}CH_2$ in H_2O and D_2O at 25.0°

R_1	R_2	Acid	k_{obsd}, s^{-1} [a]	k_{H_2O}/k_{D_2O}	k_{rel}
c-Pr 1	H	16.1% H_2SO_4 [b]	1.43×10^{-3}		
		30.4% H_2SO_4	1.87×10^{-2}	3.1	996
		30.8% D_2SO_4	5.99×10^{-3}		
c-Pr 2	Me	0.700% H_2SO_4 [c]	2.14×10^{-2}		1.8×10^{6} [d]
		0.0496 N HCl	1.03×10^{-2}	2.5	
		0.0500 N DCl	4.11×10^{-3}		
		0.100 N HCl [e]	2.04×10^{-2}		
c-Pr 3	Ph	0.500 N HCl [f]	8.19×10^{-3}		1.1×10^{5} [g]
		1.00 N HCl	2.75×10^{-2}		
		5.80% H_2SO_4	1.27×10^{-2}		
		11.2% H_2SO_4	4.50×10^{-2}	1.9	
		11.3% D_2SO_4	2.38×10^{-2}		
c-Pr 4	c-Pr	2.00×10^{-3} N HCl	2.12×10^{-2}		9.3×10^{7} [d]
		4.00×10^{-3} N HCl	4.32×10^{-2}		
		5.00×10^{-3} N DCl	1.62×10^{-2}	3.3[h]	
Ph 21	Me	0.700% H_2SO_4	1.01×10^{-5}		848[i]
Ph 22	H	30.4% H_2SO_4	1.87×10^{-5}		1.0

[a] At least two runs for each alkene were measured by ultraviolet spectroscopy with a miximum deviation of ±3%. [b] h_0 is 5.62. [c] h_0 is 0.1045. [d] Comparison via **21**. [e] h_0 is 0.1046. [f] h_0 is 0.631. [g] Comparison via **2**. [h] Calcd k_2 for 5.00×10^{-3} N HCl is 5.4×10^{-2}. [i] Rate compared to **22** at 30.4% H_2SO_4 from data in N. C. Deno, F. A. Kish, and H. J. Peterson, *J. Am. Chem. Soc.*, 87, 2157 (1965).

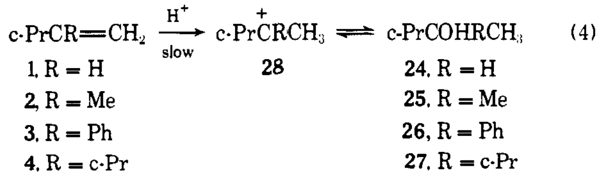
Table II. Rates of Acid-Catalyzed Hydration at 25° of Alkenes $R_1R_2C{=}CH_2$

No.	R_1	R_2	k_2, M^{-1} s^{-1}	Ref
1	c-Pr	H	0.254×10^{-3}	*a*
2	c-Pr	Me	0.200	*a*
3	c-Pr	Ph	0.130×10^{-1}	*a*
4	c-Pr	c-Pr	1.06×10^{1}	*a*
5	MeS	H	0.108×10^{-1}	*b*
6	MeO	H	0.762	*c*
7	MeO	Ph	5.45×10^{1}	*c*
8	EtO	Ph	1.20×10^{2}	*c*
9	EtO	H	1.76	*d*
10	EtO	Me	5.79×10^{2}	*d*
11	PhO	H	0.328×10^{-2}	*d*
12	PhO	Me	5.98	*d*
13	Me	Me	0.371×10^{-3}	*e*
14	EtO	EtO	10^{6}	*f*
15	*n*-Bu	H	0.108×10^{-6}	*g*
16	Et	Me	0.522×10^{-3}	*h, i*
17	CH_2Cl	Me	0.46×10^{-7}	*j*
18	*t*-Bu	Me	0.204×10^{-3}	*i, k*
19	Me	H	0.495×10^{-7}	*l, m*
20	H	H	0.612×10^{-12}	*m, n*
21	Ph	Me	0.967×10^{-4}	*a*
22	Ph	H	0.326×10^{-6}	*a*
23	MeO	c-Pr	7.46×10^{3}	*o*

[a] This work, k_2 derived from k_{obsd}/h_0 (Table I). [b] R. A. McClelland, unpublished results privately communicated ($k_{obsd} = 3.24 \times 10^{-3}$ s^{-1} in 0.273 N HCl, $h_0 = 0.300$). [c] A. J. Kresge, D. S. Sagatys, and H. L. Chen, *J. Am. Chem. Soc.*, 90, 4174 (1968); D. S. Sagatys, Ph.D. Thesis, Illinois Institute of Technology, 1970. [d] A. J. Kresge, H. L. Chen, Y. Chiang, E. Murrill, M. A. Payne, and D. S. Sagatys, *J. Am. Chem. Soc.*, 93, 413 (1971). [e] H. J. Lucas and W. F. Eberz, *ibid.*, 56, 460 (1934). [f] A. Kankaanperä and H. Tuominen, *Suom. Kemistil. B*, 40, 271 (1967). [g] K. Yates, G. H. Schmid, T. W. Regulski, D. G. Garratt, H.-W. Leung, and R. McDonald, *J. Am. Chem. Soc.*, 95, 160 (1973); h_0 for 48.7% H_2SO_4 is 1.78×10^{3}. [h] J. B. Levy, R. W. Taft, Jr., D. Aaron, and L. P. Hammett, *J. Am. Chem. Soc.*, 75, 3955 (1953). [i] Rates were measured in a gas–liquid system at 25°, and k_2 values were obtained by comparison to **13** in the same system: R. W. Taft, Jr., *J. Am. Chem. Soc.*, 74, 5372 (1952). [j] The rate was measured by Taft at 38° and reported in ref 10a; k_2 was obtained from the comparison to **13** under the same conditions. [k] R. W. Taft, Jr., E. L. Purlee, P. Riesz, and C. A. DeFazio, *J. Am. Chem. Soc.*, 77, 1584 (1955). [l] B. T. Baliga and E. Whalley, *Can. J. Chem.*, 42, 1019 (1964). [m] Extrapolated to 25° at 100 bars from rates at higher temperatures. [n] B. T. Baliga and E. Whalley, *Can. J. Chem.*, 43, 2453 (1965). [o] W. Chwang and A. J. Kresge, unpublished results privately communicated.

For correlation of the rates with substituent parameters, the rates were converted to k_2 values by dividing the observed rates by the acidity function h_0. The k_2 values and the acidity functions used are given in Tables I and II. Substituent parameters σ and σ^+ (constants for para substituents were used in all cases) were taken from the standard sources,[12] with the exception of σ for CH_2Cl (0.12),[13a] σ^+ for EtO (−0.72),[13b] σ and σ^+ for c-Pr (−0.22 and −0.44, respectively, average values),[7] and the constants for *n*-Bu (assumed the same as those for Et).[13c] Other terminal alkenes, $R_1R_2C{=}CH_2$, for which rates under comparable conditions could be located from published or unpublished sources and for which substituent constants were available, were collected and the data also compiled in Table II. Log k_2 values were plotted against $\Sigma\sigma^+$ (Figure 1) and $\Sigma\sigma$ (Figure 2) of the substituents. The slope of the least-squares correlation line shown of log k_2 vs. $\Sigma\sigma^+$ was $\rho^+ = -12.3$, with a correlation coefficient of 0.970 and an intercept of −10.1, while the correlation with $\Sigma\sigma$ gave $\rho = -20.9$ and a correlation coefficient of 0.757.

The initial products of the reactions of the cyclopropylalkenes were found to be the corresponding alcohols **24–27** (eq 4). As discussed below, the weight of evidence is that

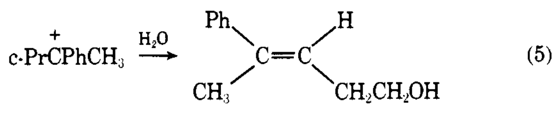


$$\text{c-PrCR}{=}\text{CH}_2 \xrightarrow[\text{slow}]{\text{H}^+} \text{c-Pr}\overset{+}{\text{C}}\text{RCH}_3 \rightleftharpoons \text{c-PrCOHRCH}_3 \qquad (4)$$

1, R = H; **2**, R = Me; **3**, R = Ph; **4**, R = c-Pr; **28**; **24**, R = H; **25**, R = Me; **26**, R = Ph; **27**, R = c-Pr

these reactions proceed through rate-determining formation of the carbonium ion intermediate **28** shown. These product studies were carried out in aqueous acid for **1** and **2**, but for solubility reasons the product studies for **3** and **4** were done in mixtures of aqueous acid and dioxane.

The product from **3** also contained (*Z*)-2-phenylpent-2-en-5-ol (**29**), as well as residual olefin. On extended reaction time, **29** became the dominant product. The acid cleavage of cyclopropylcarbinols to 4-substituted butenes is a well-known synthetic reaction,[14] and acid cleavage of **3** has been reported to yield the methyl ether of **29** when carried out in methanol,[15a] and esters of **29** when carried out in acid anhydrides.[15b] Predominant *Z* configuration has been assigned to the products,[14,15b] and the reaction presumably occurs by nucleophilic attack on the intermediate carbonium ion (eq 5).[15b] The formation of **29** explains the increasing ultraviolet absorption observed on prolonged reaction times in the kinetic determinations on **3**. The presence of both reactant **3** and rearranged alcohol **29** raise the possibility that hydration of **3** is significantly reversible. This would be less probable in the wholly aqueous solvent used for kinetic determinations.



29

The initial hydration product **27** from **4** underwent a rearrangement to 2-cyclopropyl-2-methyltetrahydrofuran (**30**), as evidenced by the isolation of **30** from the hydration reaction product or from treatment of **27** under the reaction conditions. The analogous formation of tetrahydrofurans

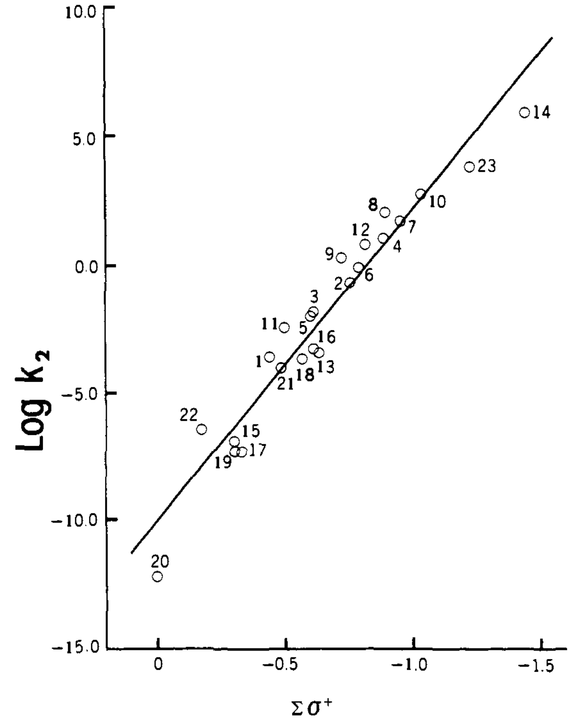


Figure 1. Correlation of rates of hydration of alkenes $R_1R_2C{=}CH_2$ with σ^+ constants.

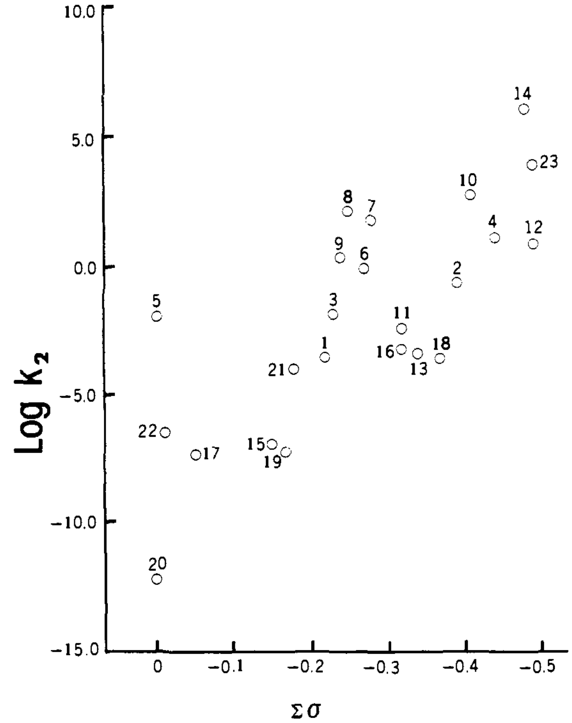
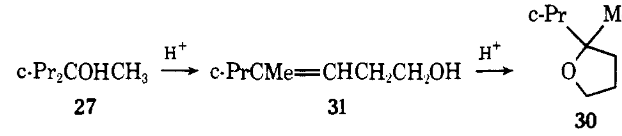


Figure 2. Correlation of rates of hydration of alkenes $R_1R_2C{=}CH_2$ with σ constants.

from acid treatment of cyclopropylcarbinols has been previously observed.[16a,c,d] Although 2-cyclopropyl-2-penten-5-ol (**31**) was not isolated from the reaction mixture, it appears likely that this material is the precursor to **30** (eq 6).



(6)

Discussion

The protonation of alkenes is a favorable case to test for the utility of substituent parameters for the correlation of aliphatic reactivities. The investigations cited in the introduction establish the A-SE2 mechanism as a prime candidate for any acid-catalyzed alkene hydration, and the restriction of the compounds examined to 1,1-disubstituted alkenes provides a further electronic bias toward such a path (eq 7).

$$R_1R_2C{=}CH_2 \xrightarrow[\text{slow}]{H^+} R_1R_2\overset{+}{C}CH_3 \qquad (7)$$

The use of Hammett-type equations to correlate aromatic reactivities has become one of the most reliable tools for the examination of organic reaction mechanisms, but the extension of this approach to aliphatic reactivities has been less successful and has commonly relied on multiparameter equations of the Taft type.[10,17] Solvation effects, conformational and other steric factors, ground-state interactions, rehybridizations during reaction, and other factors are likely to vary more in a series of aliphatic reactions than in aromatic cases. The more successful previous treatments of alkene properties in terms of Hammett constants involve physical properties[18a] and equilibria[18b] rather than reaction rates. Protonation of terminal alkenes should avoid these problems, as the site of attack remains constant and problems of steric approach control are minimized.

The results provide handsome fulfillment of these expectations. There is a surprisingly good correlation of the rates covering 18 orders of magnitude in reactivity using only the σ^+ parameters taken from the literature (Figure 1). Further, the large magnitude of ρ^+ of -12.3 is consistent with the sizable response expected for substituents adjacent to the developing positive charge in eq 7.

This result provides decisive confirmation of the A-SE2 mechanism for the acid-catalyzed hydration of terminal alkenes, as also indicated by the product studies and solvent isotope effects for the alkenes studied in this investigation. This correlation also provides a logical framework within which to consider the factors which contribute to alkene reactivities.

It is of interest to examine the possibility that the fact that two most reactive substrates (1-methoxy-1-cyclopropylethylene (**23**) and 1,1-diethoxyethylene (**14**)) lie below the correlation line results from a "saturation"[19] or "leveling"[20] of the substituent effect. Such a phenomenon may be defined as a reactivity less than that expected on the basis of additivity of substituent effects, and an example is the observed relative rates of hydrolysis of the ethers $CH_2(OEt)_2$, $CH(OEt)_3$, and $C(OEt)_4$ of 1, 680, and 66, respectively.[21] Such effects may arise from changes in mechanism due to shifts of the position of the transition state along the reaction coordinate,[21] and have been of intense recent interest in the interpretation of investigations of carbonium ions.[22] We have also observed that saturation factors are apparently operative in protonation of vinyl phosphates and are examining this system further.[1a]

In some cases, saturation factors have been attributed to steric factors,[23] and in others they have been accounted for by using the Yukawa-Tsuno equation.[11,24] It is noteworthy that in solvolytic reactions there are now at least three different systems where a developing carbonium ion is stabilized by three cyclopropyl groups, and in all cases, the cyclopropyl group effects appear to be cumulative and not saturated.[8e,16a,b]

It must be pointed out, however, that the terminal two points on the plot in Figure 1 are the least reliable experimentally. The rates for ethylene (**20**) were measured at 170-190° in 0.3-0.63 M $HClO_4$, so the value used is subject to uncertainties in the acidity function applied and the long extrapolation to 25°. 1,1-Diethoxyethylene (**14**) undergoes hydrolysis at pH 7 at 25°, so the rate constant for hydronium ion catalyzed hydrolysis is only an estimate. Thus the apparent curvature suggested by the first and last points lying below the correlation line may not be genuine. It would not be prudent to assign the apparent deviations of **14** and **23** to a definite cause such as saturation of leveling, nor to introduce additional parameters to improve the correlation. To do so might marginally improve the fit of the data but would not lead to an increase in understanding.

The point for styrene (**22**) deviates noticeably above the correlation line, and it may be said with confidence that this does not arise from uncertainty in the rate measurements. Thus styrene (**22**) is 3 times more reactive than *n*-hexene (**15**) and 6.6 times more reactive than propene (**19**), yet the σ^+ constant for phenyl (−0.18) is of considerably lower magnitude than those of methyl (−0.31) or ethyl (−0.30). The effect of phenyl in solvolytic reactions is also much greater than methyl; for example, in the esters $RCMe_2OPNB$, the phenyl/methyl rate ratio is 969.[25]

There are several possible sources of this anomaly. Ground-state stabilization effects have been considered by others[9] but should decrease the reactivity of styrene, not enhance it. It has been suggested by Noyce and Fike[13d] that cumyl chloride solvolysis gives a low value for the σ^+ of the phenyl substituent because of inhibition of coplanarity and conjugation in the *p*-phenylcumyl system due to steric interactions with the ortho hydrogens. They suggest a σ^+ value of −0.34 for the planar phenyl substituent. The steric interactions in the styrene system are less severe than in biphenyl so this approach appears more suitable for the alkene hydrations. However, the value of −0.34 overcompensates for the effect, as the correlation coefficient is reduced to 0.967, and the points for the phenyl-substituted alkenes fall below the correlation line. Nevertheless, it appears that steric causes are responsible for some of the observed deviations from the correlation.

Experimental Section

Vinylcyclopropane (**1**) and α-methylvinylcyclopropane (**2**) (Chemical Samples Co.), and 1,1-dicyclopropylethylene (4, Aldrich) were used as received. α-Cyclopropylstyrene (**3**) was prepared from cyclopropyl phenyl ketone (Aldrich) by the Wittig reaction in dimethyl sulfoxide,[26] and was purified by gas chromatography (10 ft × 0.375 in. 30% SE-30 on Chromosorb W, retention time 28 min at 170° and 50 ml He/min). Styrene (J. T. Baker) and α-methylstyrene (Eastman) were distilled before use. Elemental analyses were performed at the Gygli Microanalysis Laboratory, Toronto.

Acid Solutions. Aqueous sulfuric acid solutions were prepared by diluting concentrated reagent with distilled water. Concentrations determined by titration were converted to per cent acid by use of a published table.[27] Aqueous HCl solutions were obtained by dilution of commercial reagents and were standardized by titration. Deuterated sulfuric acid solutions were obtained by diluting concentrated deuteriosulfuric acid (Diaprep) with D_2O (Merck Sharp and Dohme). Deuterated hydrochloric acid was prepared by dilution of ordinary reagent acid with D_2O. The dilution was such that the solutions obtained contained less than 0.5% protium.

Kinetics. Stock solutions of the aliphatic olefins (10^{-2}–10^{-3} M) in 95% ethanol were prepared by weighing the olefins into 3-ml volumetric flasks. The acid solutions (3.0 ml) in 1-cm uv cells were equilibrated in the cell compartment of the Cary 16 spectrophotometer thermostated at 25.0°. The olefin solution (10 μl) was injected into the cell which was shaken, and the decrease of the ultraviolet maximum was monitored vs. time. The positions of the maxima (nm) in aqueous solution compared to literature values for cyclohexane solutions (in parentheses)[28] were **1**, 196 (192); **2**, 196 (196); and 4, 205 (201).

α-Cyclopropylstyrene (**3**) dissolved slowly in water, so a different technique was used. A 10-μl portion of a 10^{-3} M solution of the olefin in 95% ethanol was added to 2 ml of water in the cell and kept for 20 min until the absorption at 245 nm was constant. Then 1 ml of acid solution was injected and the cell shaken; the reaction was followed as before (λ_{max} (H_2O) 245 nm, lit.[29] λ_{max} (EtOH) 242 nm).

Product Studies. Authentic samples of methylcyclopropylcarbinol (**24**) and dimethylcyclopropylcarbinol (**25**) were prepared from methyl cyclopropyl ketone (Aldrich) by $NaBH_4$ reduction and reaction with methyllithium, respectively. Methyldicyclopropylcarbinol (**27**) and methylphenylcyclopropylcarbinol (**26**) were prepared by the addition of methyllithium to dicyclopropyl ketone and methylmagnesium iodide to cyclopropyl phenyl ketone, respectively.

The products from vinylcyclopropane (**1**) and α-methylvinylcyclopropane (**2**) were determined by stirring 2 mmol of the olefins with 20 ml of 30.4% and 0.700% H_2SO_4, respectively, for 30 min (50 half-lives). The solutions were initially heterogeneous, and with **1** remained so. Residual **1** was allowed to evaporate and the yield calculated on the weight alkene absorbed. The solutions were neutralized by $NaHCO_3$ and extracted with ether overnight. After removal of the ether, the products were analyzed by VPC (10 ft × 0.375 in. 30% SE-30, column 88°, injector 136°) using standard solutions for calibration. The carbinol **24** partially decomposed to **1** under these conditions but was the only significant volatile product and was present in 20% yield. The yield of **25** from **2** was 85%.

α-Cyclopropylstyrene (**3**, 0.16 g) was kept 24 h in a solution composed of 50 ml of dioxane and 25 ml of 2 N $HClO_4$. The solution was poured into a Na_2CO_3 solution and extracted twice with pentane. The combined pentane layers were washed once with Na_2CO_3, twice with H_2O, and once with saturated NaCl solution and the solvent was removed. The residue was analyzed by VPC (6 ft × 0.25 in. SE-30, column 120°, injector 180°, He 60 ml/min) and found to contain 13% residual **3**, 23% of methylphenylcyclopropylcarbinol (**26**), and 64% of (*Z*)-2-phenylpent-2-en-5-ol (**29**). Decomposition occurred at higher column temperatures. The products were isolated from the same column and each identified by its spectral characteristics: **29** gave mass spectrum (70 eV) *m/e* 162 (M^+) and ^1H NMR (CCl_4) δ 2.00 (broad s, 3, Me), 2.36 (broad quartet, 2, J = 7 Hz, allyl CH_2), 2.77 (s, 1, OH), 3.62 (t, 2, J = 7 Hz, CH_2O), 5.68 (broad t, 1, J = 7 Hz, vinyl H), and 7.1 (m, 5, aryl). Treatment of **26** (0.19 g) with 50 ml of dioxane and 25 ml of 1 N HCl for 1.5 h and work-up gave a mixture containing 20% **3**, 40% recovered **26**, and 40% of 5-chloro-(*Z*)-2-phenyl-2-pentene: mass spectrum (70 eV) *m/e* 180 (M^+); NMR (CCl_4) δ 2.04 (broad s, 3, Me), 2.65 (broad quartet, 2, J = 7 Hz, allyl CH_2), 3.52 (t, 3, J = 7 Hz, CH_2Cl), 5.72 (broad t, 1, J = 7 Hz, vinyl H), and 7.12 (s, 5, aryl).

Dicyclopropylethylene (4, 0.065 g) was kept 2.5 min in a solution composed of 50 ml of dioxane and 250 ml of 1 N $HClO_4$. The solution was worked up and analyzed by VPC (6 ft × 0.25 in. SE-30, column 80°, injector 190°, He 60 ml/min) and found to contain 80% of methyldicyclopropylcarbinol (**27**) and 20% of 2-cyclopropyl-2-methyltetrahydrofuran (**30**): mass spectrum (70 eV) *m/e* (rel int) 126 (M^+, 6), 111 ($M^+ - CH_3$, 50), 85 ($M^+ - C_3H_5$, 40), 58 ($C_3H_6O^+$, 100); ^1H NMR (CCl_4) δ 0.2–0.8 (m, 5, c-Pr), 1.16 (s, 3, Me), 1.8 (m, 4, CH_2CH_2), and 3.7 (m, 2, CH_2O); and no OH or olefin signals in the infrared. Anal. Calcd for $C_8H_{14}O$ (126.20): C, 76.14; H, 11.18. Found: C, 75.89; H, 11.19.

Reaction of **4** as above for 8 min gave a 10:1 ratio of **30** and **27** in the product, and 7 h reaction time gave **30** as essentially the only product. Treatment of **27** under the reaction conditions for 38 min resulted in almost exclusive conversion to **30**.

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The Stereochemistry of Free Radical Eliminations on β-Phenylthio Radicals

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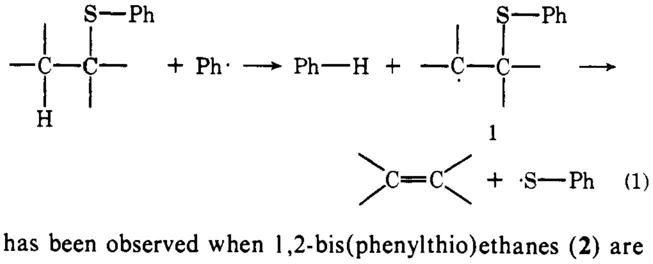
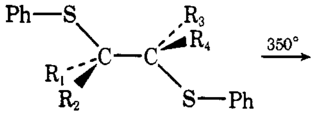
Abstract: Tributyltin radicals have been allowed to react with *erythro*- and *threo*-2-bromo-3-phenylthiobutane (**4a** and **4b**) to generate β-phenylthio radicals (**1**). The intermediate **1** eliminates thiophenoxy radical to form the 2-butenes nonstereospecifically. The lack of stereospecificity coupled with the fact that no 2-phenylthiobutane, the normal reduction product, is formed implies that the barrier to rotation in **1** is <7.2 kcal/mol and that stabilization of the radical by sulfur bridging is unimportant. The relative rates of reaction of **4a** and **4b**, as well as those of *cis*- and *trans*-1-bromo-2-phenylthiocyclohexane (**7a** and **7b**), with tributyltin radicals have been measured. The results of these experiments (k_{4a}/k_{4b} = 1.12 ± 0.13 and k_{7b}/k_{7a} = 1.57 ± 0.28) indicate that anchimeric assistance of bromine abstraction by sulfur is unimportant.

The elimination of a thiophenoxy radical from a β-phenylthio radical, **1**, is well documented in the literature. For example, Kampmeier and coworkers have observed that reaction of phenylthioalkanes with phenyl radicals generates **1**, which subsequently eliminates thiophenoxy radical to form an alkene (eq 1).[1] A similar free radical elimination

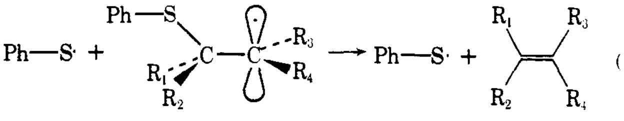


(1)

has been observed when 1,2-bis(phenylthio)ethanes (**2**) are pyrolyzed.[2,3] We have shown that elimination of phenyl disulfide from **2a** and **2b** proceeds with a predominance of anti stereochemistry (eq 2).[3]



2a, $R_1 = R_4 = H$; $R_2 = R_3 = Me$
b, $R_1 = R_3 = H$; $R_2 = R_4 = Me$



(2)

1a, $R_1 = R_4 = H$; $R_2 = R_3 = Me$
b, $R_1 = R_3 = H$; $R_2 = R_4 = Me$

major product