

in the probe to the temperature at which the rate was to be measured. Between 20 and 30 100-Hz sweep-width spectra were measured over a period of up to 2 hr at each of three temperatures,  $-57$ ,  $-54$ , and  $-52^\circ$ . The relative concentrations were determined for each scan using both peak heights and integrated peak intensities obtained by cutting out peaks on Xerox copies of the spectra and weighing them. The resulting mole fractions and times were then fitted, using a double precision linear least-squares computer program, to the rate equation for a first-order reaction,

$$\frac{-K}{K+1} \ln [1 - X_B(1 + 1/K)] = kt$$

where  $K$  is the equilibrium constant,  $X_B$  is the mole fraction of the low-field isomer, and  $k$  is the rate constant for isomerization. The equilibrium constant used was obtained by extrapolation from a plot of equilibrium constant vs. temperature. The rates obtained were:  $-57^\circ$ ,  $k = (1.69 \pm 0.05) \times 10^{-4} \text{ sec}^{-1}$ ,  $-54^\circ$ ,  $k = (4.53 \pm 0.16) \times 10^{-4} \text{ sec}^{-1}$ , and  $-52^\circ$ ,  $k = (7.11 \pm 0.19) \times 10^{-4} \text{ sec}^{-1}$ . The rates in the high-temperature region ( $16$ – $57^\circ$ ) were determined

by CLS. Arrhenius parameters obtained using high-temperature ( $16$ – $57^\circ$ ) rates only were:  $E_a = 19.4 \pm 0.8 \text{ kcal/mol}$ ;  $\log A = 15.0 \pm 0.6 \text{ sec}^{-1}$ ;  $\Delta H^\ddagger = 18.8 \pm 0.8 \text{ kcal/mol}$ ;  $\Delta S^\ddagger = 8 \pm 3 \text{ eu}$ . The correlation coefficient was  $-0.993$ . Arrhenius parameters obtained using both high- and low-temperature rates ( $-57$  to  $57^\circ$ ) were:  $E_a = 16.2 \pm 0.3 \text{ kcal/mol}$ ;  $\log A = 12.8 \pm 0.2 \text{ sec}^{-1}$ ;  $\Delta H^\ddagger = 15.7 \pm 0.3 \text{ kcal/mol}$ ;  $\Delta S^\ddagger = -2 \pm 1 \text{ eu}$ . The correlation coefficient was  $-0.998$ .  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were calculated using the equations given below. The values obtained from the two methods for calculating  $\Delta S^\ddagger$  were in good agreement:  $\Delta H^\ddagger = E_a - RT$ ;  $\Delta S^\ddagger = R \ln(Ah/k_bT) - R$ ;  $\Delta S^\ddagger = (\Delta H^\ddagger - \Delta G^\ddagger)/T$ . The entropy and enthalpy of activation were also calculated using a linear least-squares computer program of the Eyring equation

$$\ln(k/T) = \ln(k_b/h) + \Delta S^\ddagger/R - \left(\frac{\Delta H^\ddagger}{R}\right)\left(\frac{1}{T}\right)$$

These results were identical with those obtained from Arrhenius parameters ( $\Delta H^\ddagger = 15.6 \pm 0.3 \text{ kcal/mol}$ ;  $\Delta S^\ddagger = -1.6 \pm 1 \text{ eu}$ ).

## The Acid-Catalyzed Isomerization of *cis*-1-Phenyl-1,3-butadiene and *cis*-1-Methyl-3-phenylallyl Alcohol<sup>1</sup>

Y. Pocker\*<sup>2</sup> and Martin J. Hill<sup>3</sup>

Contribution from the Department of Chemistry,  
University of Washington, Seattle, Washington 98105.  
Received June 25, 1970

**Abstract:** The kinetics of the acid-catalyzed isomerization of *cis*-1-phenyl-1,3-butadiene (**1**) and *cis*-1-methyl-3-phenylallyl alcohol (**2**) to the corresponding trans compounds in aqueous sulfuric acid as well as in 40% aqueous dioxane containing perchloric acid have been investigated. Both reactions give good pseudo-first-order kinetics, and plots of  $\log k$  vs.  $-H_0$  give good straight lines. The rate of isomerization of **1** in deuteriosulfuric acid is slower by a factor of 2.24–3.15 than in aqueous sulfuric acid, although deuterium incorporation occurs exclusively at the terminal carbon atom. The rate of isomerization of **2** is accelerated in deuteriosulfuric acid by a factor of 2.5 over the aqueous acid, and there is no deuterium incorporation into the molecule except for the hydroxyl proton. The loss of  $^{18}\text{O}$  label from labeled **2** occurs at the same rate as isomerization to trans alcohol, indicating that the loss of water from protonated **2** is rate determining in the isomerization and there is no detectable return to starting material. Similarly, the protonation of **1** to give the *cis* carbonium ion is found to be rate determining. In each case, rapid rotation about the  $\text{C}_1$ – $\text{C}_2$  bond converts the *cis* carbonium ion directly to the trans ion before attack by solvent can occur. Thus, even under kinetic control, all products are derived from the trans carbonium ion. This is the first case of a *cis* allylic cation that is not stable with respect to *cis*–*trans* isomerization in aqueous solution. Due consideration to the energetic requirements is given in the discussion of these processes.

The present paper is a continuation of a kinetic and mechanistic study of the reactions of *cis*- and *trans*-1-phenyl-1,3-butadiene and their water adducts in aqueous acids.<sup>4,5</sup> It will be shown below that *cis*-1-phenyl-1,3-butadiene (**1**) and *cis*-1-methyl-3-phenylallyl alcohol (**2**) isomerize readily in moderately concentrated acids to give ultimately the same equilibrium mixture that is obtained from the corresponding trans compounds in the same media. A survey of the literature pertaining to such processes shows precedents for two types of behavior.

The *cis*–*trans* isomerization of allylic alcohols has been studied by Young and Franklin,<sup>6</sup> who followed the

acid-catalyzed interconversion of  $\alpha$ -methylallyl alcohol and *cis*- and *trans*-crotyl alcohols. They observed that starting from either isomer of crotyl alcohol the vapor phase chromatography (vpc) peak corresponding to  $\alpha$ -methylallyl alcohol appeared before that of the other isomer, indicating that  $\alpha$ -methylallyl alcohol is an intermediate in the isomerization. All three alcohols yielded the same product mixture (66.28%  $\alpha$ -methylallyl alcohol, 24.46% *cis*-, and 3.73% *trans*-crotyl alcohol) under the same conditions. The rate of disappearance of each alcohol was followed by vpc, and on the basis of these rates a theoretical equilibrium distribution of products was calculated. The observed results agreed best with the product distribution predicted for the following mechanism. Thus, it was concluded that the *cis*- and *trans*-allylic carbonium ions are stable with respect to geometrical isomerization, a conclusion reached with other allylic systems.<sup>7</sup> By

(7) W. G. Young, S. H. Sharman, and S. Winstein, *ibid.*, **82**, 1376

(1) Taken in part from the Ph.D. Thesis of Martin J. Hill, University of Washington, Seattle, Wash., 1970.

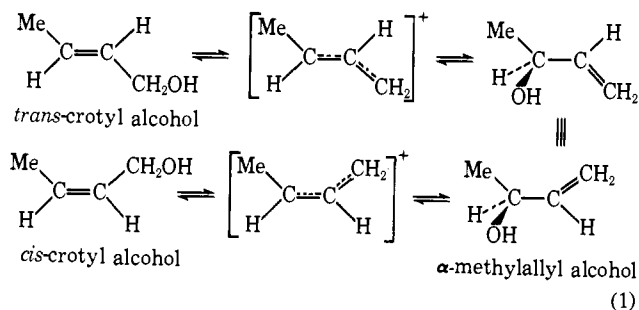
(2) To whom inquiries should be addressed.

(3) Minnesota Mining and Manufacturing Co. Fellow, 1969–1970.

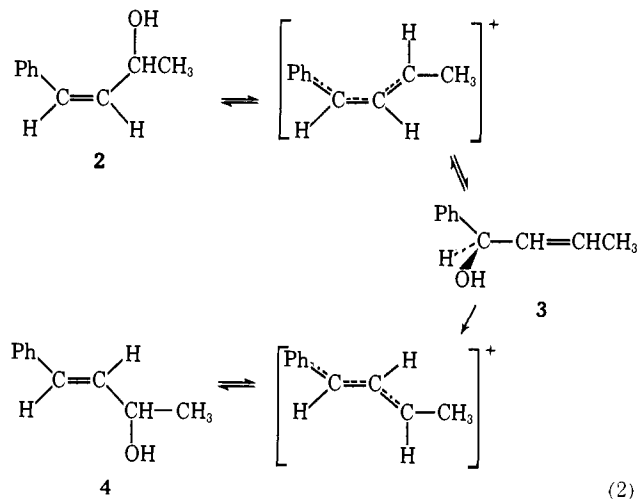
(4) Y. Pocker and M. J. Hill, *J. Amer. Chem. Soc.*, **91**, 3243 (1969).

(5) Y. Pocker and M. J. Hill, *ibid.*, **91**, 7154 (1969).

(6) W. G. Young and J. S. Franklin, *ibid.*, **88**, 785 (1966).

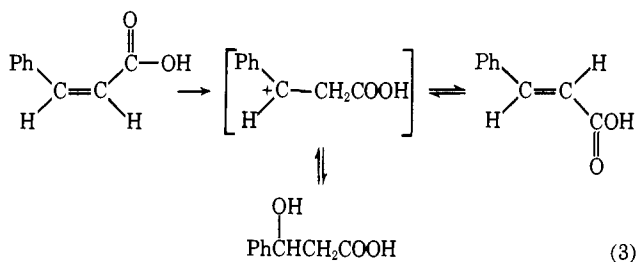


analogy with these cases, one might propose the following mechanism for the isomerization of 2.

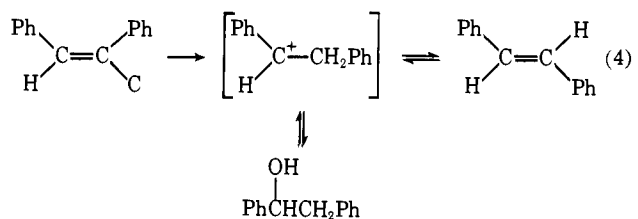


The intermediate 1-phenyl-3-methylallyl alcohol (3) has indeed been shown to isomerize rapidly to give *trans*-1-methyl-3-phenylallyl alcohol (4),<sup>4</sup> so this mechanism is a distinct possibility.

However, the acid-catalyzed isomerization of *cis*-cinnamic acid was shown to proceed *via* hydration of the styryl double bond by Noyce, *et al.*<sup>5</sup> The isomeriza-



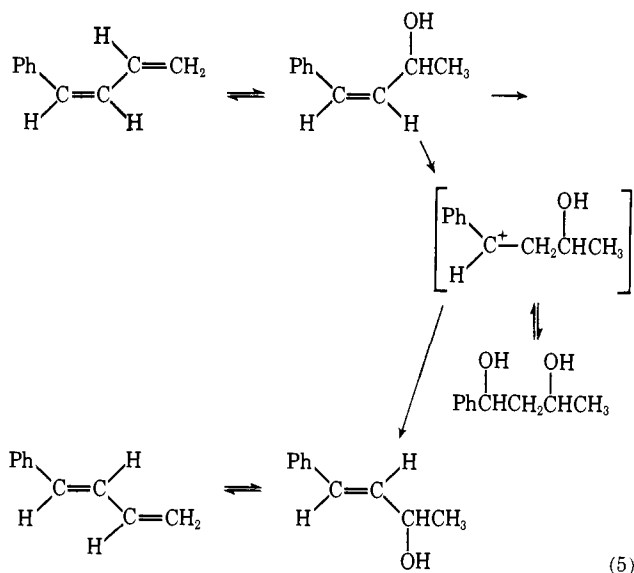
tion of *cis*-stilbene was shown to follow along similar lines (eq 4). Then by analogy with these systems a



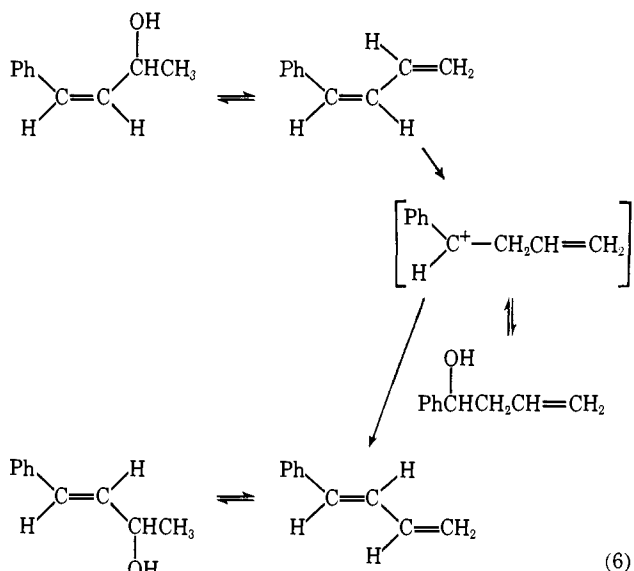
reasonable alternative for the isomerizations of 1 and 2 would be either hydration of the double bond of 2

(1960); P. D. Sleezer, S. Winstein, and W. G. Young, *J. Amer. Chem. Soc.*, **85**, 1890 (1963).

(8) D. S. Noyce, P. A. King, and F. B. Kirby, *ibid.*, **84**, 1632 (1962); D. S. Noyce and H. S. Avarbock, *ibid.*, **84**, 1644 (1962); D. S. Noyce, H. S. Avarbock, and W. L. Reed, *ibid.*, **84**, 1647 (1962).



or hydration of the styryl double bond of 1.



In order to distinguish between these three possibilities (eq 2, 5, and 6), a kinetic study of the isomerizations of 1 and 2 was carried out.

## Experimental Section

**Preparation of Materials.** *cis*-1-Phenyl-1,3-butadiene (1) was prepared by the method of Grummitt and Christoff.<sup>9</sup> The ultraviolet spectrum of the product showed no trace of the *trans* alkene (5) and agreed with that reported,  $\lambda_{\max}$  266 m $\mu$  ( $\epsilon$  16,700) in water.

*cis*-1-Methyl-3-phenylallyl alcohol (2) was prepared by the method of Braude and Coles<sup>10</sup> using a Lindlar catalyst<sup>11</sup> partially poisoned with quinoline for the hydrogenation step. The product showed no traces of the saturated alcohol or the starting material (by nmr), and its ultraviolet spectrum ( $\lambda_{\max}$  240 m $\mu$ ,  $\epsilon$  12,000) agreed with that reported.

*cis*-1-Methyl-3-phenylallyl alcohol-<sup>18</sup>O was prepared in a manner exactly analogous to the preparation of 2 using <sup>18</sup>O-labeled acetaldehyde. Acetaldehyde (8 g) was stirred with 20 g of <sup>18</sup>O-enriched water (1.92 atom % excess), extracted with ether, and dried over calcium sulfate, yielding acetaldehyde-<sup>18</sup>O (1.4 atom % excess). The product *cis*-1-methyl-3-phenylallyl alcohol-<sup>18</sup>O also had 1.4 atom % excess <sup>18</sup>O label.

(9) O. Grummitt and F. J. Christoff, *ibid.*, **73**, 3479 (1951).

(10) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2085 (1951).

(11) H. Lindlar and R. Dubuis, *Org. Syn.*, **46**, 89 (1966).

1-Phenyl-3-buten-1-ol (7) was prepared by the action of allylmagnesium bromide<sup>12</sup> on benzaldehyde. The product had bp 42–44° (3 mm) (lit.<sup>13</sup> 111–112° at 13 mm). The nmr was consistent with this structure.

1-Phenyl-1,3-butanediol (6). The crotonophenone synthesis of Pasteur, *et al.*,<sup>14</sup> was interrupted after drying of the ether solution of phenyl 2-hydroxypropyl ketone, which was reduced with lithium aluminum hydride to give 6, bp 150° (5 mm).

The remaining compounds were prepared as previously described.<sup>4,5</sup> The kinetic methods were described in detail earlier.<sup>4</sup> As before, all rates were carried out at 25° unless otherwise noted. Cylindrical cells of 10-cm path length were used for monitoring the disappearance of 1 in aqueous acid, because of its limited solubility in water.

## Results

To allow comparison with previous studies, including the use of solvent isotope effects and <sup>18</sup>O-exchange rates, the isomerizations of 1 and 2 were carried out in two solvent systems: aqueous sulfuric acid and 40% aqueous dioxane with perchloric acid as catalyst. Both reactions proceed smoothly in each solvent, and pseudo-first-order plots give good straight lines for at least 2 half-lives,<sup>15</sup> with the results shown in Tables I and II. Plots of log *k* vs.  $-H_0$ <sup>16</sup> give good straight lines in each case (Figure 1), with slopes of 1.44 and 1.50 for the isomerization of 1 in aqueous sulfuric acid and in perchloric acid–40% dioxane, respectively, and with slopes of 1.15 and 1.35 for the isomerization of 2 in aqueous sulfuric acid and in perchloric acid–40% dioxane, respectively.

(12) O. Grummitt, E. P. Budewitz, and C. C. Chudd, "Organic Syntheses," Coll. Vol. IV, Wiley, New York, N. Y., 1963, p 748.

(13) M. Gaudemar, *Bull. Soc. Chim. Fr.*, 974 (1962).

(14) A. Pasteur, H. Riviere, and B. Tchonbar, *ibid.*, 2328 (1965).

(15) It was noted previously that the hydration of *trans*-1-phenyl-1,3-butadiene in 40% dioxane solvent containing between 2.5 and 5 *M* perchloric acid is followed by a subsequent reaction that slowly destroys the product equilibrium mixture, most likely the hydration of the C<sub>1</sub>–C<sub>2</sub> double bond to give 1-phenyl-1,3-butanediol (6). Indeed, this process occurs at a rate comparable to that of the hydration of styrene in this medium. This is faster than the isomerization of 1 by a factor of about five, and the situation may be treated kinetically as a pair of consecutive first-order reactions. Since the reaction was followed spectrophotometrically, all species in solution are monitored simultaneously, and it may be shown that at time *t* the absorbance of the solution is given by

$$A = \epsilon_6 A_0 + A_0 e^{-k_1 t} (\epsilon_1 - \epsilon_6) + \frac{A_0 k_1}{k_3 - k_1} (\epsilon_4 + \epsilon_5 K_2 - \epsilon_6 - \epsilon_6 K_2) (e^{-k_1 t} + e^{-k_3 t})$$

This is not integrable as it stands, but knowing that  $k_3 \approx 5k_1$  allows further simplification. As *t* increases,  $(e^{-k_1 t} + e^{-5k_1 t})$  becomes equivalent to  $e^{-k_1 t}$ , because  $e^{-5k_1 t}$  decreases far more rapidly than  $e^{-k_1 t}$ . Thus after about 1 half-life the expression for absorbance becomes

$$A = \epsilon_6 A_0 + \left[ A_0 (\epsilon_1 - \epsilon_6) + \frac{A_0 k_1}{k_3 - k_1} (\epsilon_4 + \epsilon_5 K_2 - \epsilon_6 - \epsilon_6 K_2) \right] e^{-k_1 t}$$

which is the expression for a first-order process with rate constant  $k_1$ . This treatment predicts curvature for about 1 half-life and then a good straight line whose slope is the rate constant for the disappearance of 1. This behavior is followed exactly by the experimental observations, and the rate constants for the linear portions (at least 2 further half-lives) are recorded in Table I. Note that in aqueous sulfuric acid this complication does not arise, and the reaction is quite clean.

(16)  $H_0$  values for H<sub>2</sub>SO<sub>4</sub> solutions were taken from M. A. Paul and F. A. Long (*Chem. Rev.*, 57, 1 (1957)) and for HClO<sub>4</sub>–40% dioxane solutions from C. A. Bunton, J. B. Ley, A. J. Rhind-Tutt, and C. A. Vernon (*J. Chem. Soc.*, 2327 (1955)).

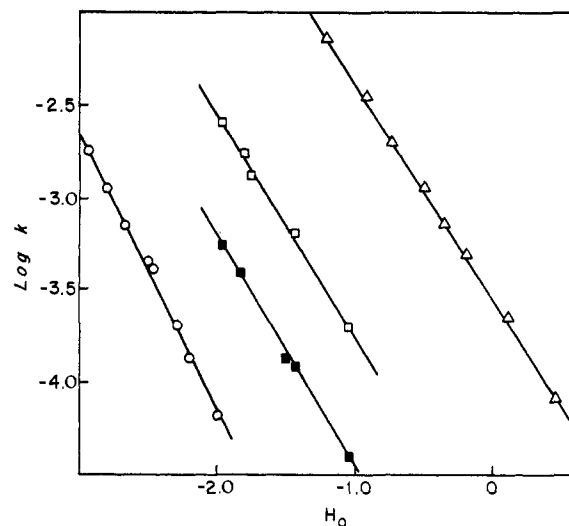


Figure 1. Plots of log *k* vs.  $H_0$  for the isomerization of 1 (O), the hydration of 5 (■), the dehydration of 4 (□), and the isomerization of 2 (Δ), all at 25° in aqueous sulfuric acid.

The isomerization of 1 was carried out at 15, 25, 35, and 45°, with results as in Table III. Plots of ln *k* vs.

Table I. Pseudo-First-Order Rate Constants for the Isomerization of *cis*-1-Phenyl-1,3-butadiene at 25°

Acid, <i>M</i>	10 <sup>4</sup> <i>k</i> , sec <sup>-1</sup>	$H_0$	–log <i>k</i>
Aqueous H <sub>2</sub> SO <sub>4</sub>			
6.31	17.8	–2.93	2.750
6.08	11.3	–2.80	2.947
5.81	7.2	–2.66	3.140
5.51	4.5	–2.51	3.347
5.45	4.1	–2.48	3.387
5.01	2.3	–2.29	3.644
4.80	1.36	–2.20	3.867
4.33	0.74	–2.00	4.131
HClO <sub>4</sub> in 40% Aqueous Dioxane			
5.07	6.1	–2.30	3.215
4.68	2.54	–2.05	3.595
4.56	2.05	–1.97	3.688
4.28	0.96	–1.79	4.016
4.07	0.64	–1.65	4.194
4.00	0.53	–1.61	4.275
3.62	0.25	–1.36	4.604
3.49	1.88	–1.28	4.726

Table II. Pseudo-First-Order Rate Constants for the Isomerization of *cis*-1-Methyl-3-phenylallyl Alcohol at 25°

Acid, <i>M</i>	10 <sup>4</sup> <i>k</i> , sec <sup>-1</sup>	$H_0$	–log <i>k</i>
Aqueous H <sub>2</sub> SO <sub>4</sub>			
2.66	72	–1.22	2.143
2.13	35	–0.93	2.456
1.79	20.6	–0.74	2.686
1.41	11.6	–0.52	2.935
1.13	7.5	–0.36	3.125
0.89	5.1	–0.20	3.292
0.53	2.27	+0.09	3.644
0.25	0.84	+0.44	4.076
HClO <sub>4</sub> in 40% Aqueous Dioxane Solvent			
2.91	110	–0.90	1.959
2.32	35.5	–0.49	2.450
1.96	16.2	–0.29	2.791
1.74	10.0	–0.14	3.000
1.39	5.5	+0.11	3.260
1.12	2.7	+0.30	3.569
0.94	1.69	+0.46	3.772
0.61	0.62	+0.86	4.208

**Table III.** Activation Parameter Data for the Isomerization of *cis*-1-Phenyl-1,3-butadiene

Acid, <i>M</i>	Temp, °C	$10^4k$ , sec <sup>-1</sup>	$-\ln k$	$10^3/T$ , °K <sup>-1</sup>
Aqueous H <sub>2</sub> SO <sub>4</sub>				
5.01	20	1.44	8.845	3.411
4.33		0.44	10.031	
5.01	25	2.3	8.390	3.354
4.33		0.74	9.512	
5.01	35	6.8	7.293	3.245
4.33		2.16	8.440	
5.01	45			3.143
4.33		5.5	7.505	
HClO <sub>4</sub> in 40% Aqueous Dioxane				
4.68	15	0.67	9.614	3.470
4.28		0.28	10.498	
4.68	25	2.5	8.278	3.354
4.28		0.96	9.246	
4.68	35	6.8	7.293	3.245
4.28		3.1	8.069	
4.68	45	18.4	6.298	3.143
4.28		8.5	7.070	

$1/T$  gave good straight lines with slopes  $9340^\circ\text{K}^{-1}$  in aqueous sulfuric acid and  $10270^\circ\text{K}^{-1}$  in perchloric acid-40% dioxane. From these slopes the activation energy in aqueous sulfuric acid was calculated to be  $18.5 \text{ kcal mol}^{-1}$  and in the mixed solvent  $20.4 \text{ kcal mol}^{-1}$ .

This reaction was also followed in deuteriosulfuric acid, in which solvent the rates are slower than in aqueous sulfuric acid. This retardation in rate is large enough (Table IV) to be considered a primary isotope

**Table IV.** Pseudo-First-Order Rate Constants for the Isomerization of *cis*-1-Phenyl-1,3-butadiene in Deuteriosulfuric Acid at 25°

Acid, <i>M</i>	$10^4k_D$ , sec <sup>-1</sup>	$10^4k_H$ , <sup>a</sup> sec <sup>-1</sup>	$k_D/k_H$
6.18	4.1	12.9	3.15
5.40	1.52	3.9	2.57
5.28	1.30	3.1	2.38
4.84	0.91	2.04	2.24

<sup>a</sup> Rate constants for the reaction in the same molarity of aqueous sulfuric acid, extrapolated from the data in Table I.

effect, indicating a rate-determining proton transfer.<sup>17</sup> An additional run was carried out with dry dioxane added to enable a larger substrate concentration to be used. At ten half-lives for the isomerization, the reaction was quenched by adding aqueous sodium hydroxide solution until the mixture was no longer acidic, and the products were extracted from solution with ether. After drying and evaporation of the ether, an nmr spectrum of the products was taken. Comparison of this spectrum with that obtained from a sample of the *trans* alkene treated identically shows that no deuterium had been incorporated into the styryl double bond of the products during isomerization, though deuterium incorporation at the terminal carbon was observed, as would be expected.

Turning to the isomerization of **2**, this reaction is much faster than the equilibration of **4** and **5**. On disappearance of the spectrum of **2**, a spectrum builds up that is identical with the spectrum of the *trans*-alcohol **4**. Subsequently a change occurs at a slower

(17) K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

rate leading to the equilibrium mixture of **4** and **5**. Since the spectra of **2** and **4** overlap somewhat, it was judged most convenient to follow this reaction at the  $\lambda_{\text{max}}$  of **4** ( $252 \text{ m}\mu$ ), as the extinction coefficients of the two species have the largest difference at this point. Monitoring the complete ultraviolet spectrum during this reaction gives no detectable absorption due to other species, indicating that **4** is the first stable product obtained from **2**.

Runs were carried out over a temperature range of  $15\text{--}45^\circ$  and the results are summarized in Table V.

**Table V.** Activation Parameter Data for the Isomerization of *cis*-1-Methyl-3-phenylallyl Alcohol

Acid, <i>M</i>	Temp, °C	$10^4k$ , sec <sup>-1</sup>	$-\ln k$	$10^3/T$ , °K <sup>-1</sup>
Aqueous H <sub>2</sub> SO <sub>4</sub>				
0.88	15	1.27	8.971	3.470
1.13		2.0	8.517	
0.88	25	5.0	7.601	3.354
1.13		7.5	7.195	
0.88	35	17.8	6.331	3.245
1.13		27.5	5.896	
0.88	45	51	5.279	3.143
1.13		76	4.880	
HClO <sub>4</sub> in 40% Aqueous Dioxane				
0.94	15	0.42	10.078	3.470
1.39		1.15	9.070	
0.94	25	1.69	8.685	3.354
1.39		5.5	7.505	
0.94	35	5.6	7.433	3.245
1.39		17.4	6.354	
0.94	45	20.3	6.200	3.143
1.39		58	5.150	

Plots of  $\ln k$  vs.  $1/T$  gave good straight lines of slope  $11200^\circ\text{K}^{-1}$  in aqueous sulfuric acid and  $11900^\circ\text{K}^{-1}$  in perchloric acid-40% dioxane, and hence activation energies were calculated to be  $22.2 \text{ kcal mol}^{-1}$  and  $23.6 \text{ kcal mol}^{-1}$ , respectively.

This reaction was also studied in deuteriosulfuric acid (0.247–1.34 *M*), and the results are given in Table VI.

**Table VI.** Pseudo-First-Order Rate Constants for the Isomerization of *cis*-1-Methyl-3-phenylallyl Alcohol in Deuteriosulfuric Acid at 25°

Acid, <i>M</i>	$10^4k_D$ , sec <sup>-1</sup>	$10^4k_H$ , sec <sup>-1</sup>	$k_D/k_H$
1.34	27.5	11.0	2.50
0.85	11.5	4.6	2.50
0.51	5.2	2.04	2.55
0.247	2.06	0.84	2.45

<sup>a</sup> Rate constants in the same molarity of aqueous sulfuric acid at 25°, extrapolated from the data in Table II.

The rate is strongly increased in deuterated media ( $k_D/k_H = 2.5$ ), indicating a preequilibrium protonation of the substrate prior to the rate-determining step. A fifth run was carried out with dioxane added and a larger concentration of substrate, and the reaction was quenched with base after 10 half-lives for isomerization. After extraction from the solution, the nmr spectrum of the product was taken, and was found to be identical with the spectrum of **4**. Thus, no deuterium incorporation into the molecule of **2** whatsoever had occurred (except for the labile hydroxyl proton).

A sample of  $^{18}\text{O}$ -labeled **2** was prepared and the rate of  $^{18}\text{O}$  loss to the solvent water during the isomerization was studied. This method<sup>4</sup> involves extraction of both starting material and product from solution in aliquots which are quenched in base. As the isomerization proceeds, the proportion of starting material and product in the aliquot changes, and the label content of each aliquot changes. If the rate constant for decrease in label is slower than isomerization, this reflects the formation of labeled product. Similarly, if the rate of loss of label is faster than isomerization, the return to unlabeled starting material is indicated. For the present case, 0.96 M perchloric acid–40% aqueous dioxane at 25°, the isomerization rate constant ( $1.71 \times 10^{-4} \text{ sec}^{-1}$ ) and the rate constant for loss of  $^{18}\text{O}$  label ( $1.74 \times 10^{-4} \text{ sec}^{-1}$ ) are the same (Figure 2). Thus within experimental error (5%) exchange of oxygen with solvent only occurs concurrently with isomerization.

The rate of oxygen exchange between product and water is fast under these conditions,<sup>4</sup> so the most significant consequence of the above experiment is that return from carbonium ion to cis alcohol does not compete with further reaction of the carbonium ion. Thus if the cis carbonium ion is generated in solution by another route it cannot collapse with water to give **2**.

Since in eq 4 and 5 the compounds **6** and **7** were proposed as intermediates in the isomerizations, they were prepared and subjected to the conditions in which the isomerizations proceed smoothly. In both solvents they failed to produce an ultraviolet spectrum similar to that obtained from **1** or **2**, so they must be ruled out as intermediates.

## Discussion

Considering the isomerization of the alcohol **2** first, it should be noted that no traces of the absorptions that would be expected from the cis or trans alkenes appeared in the ultraviolet spectrum of the reaction mixture. Since these alkenes are relatively stable under the mild conditions in which **2** isomerizes, one would expect large absorbances at their respective absorption maxima if they were generated during the isomerization. Thus it is established that the immediate reaction product is the trans-alcohol **4**. This rules out the mechanism in eq 6, as this requires that **1** be an intermediate.

The postulated mechanism in eq 5 may be eliminated from consideration by the results of runs carried out in deuterio acid. This proposed scheme has a rate-determining proton transfer to the carbon atom at the 2 position. The expected manifestation of such a reaction is a retardation of rate in deuterio acid<sup>17</sup> and deuterium incorporation into the product molecule, neither of which were observed. In fact, the rate is accelerated in deuterated media, indicating a preequilibrium proton transfer to the substrate.<sup>17</sup> Since incorporation of deuterium is ruled out, the most likely position of protonation is on the oxygen of the hydroxyl group.

The  $^{18}\text{O}$ -exchange experiment demonstrates that loss of water from the protonated alcohol is no faster than isomerization, so it is proposed that this is the rate-determining step in the isomerization. The mechanism of isomerization of the cis carbonium ion formed will be discussed below.

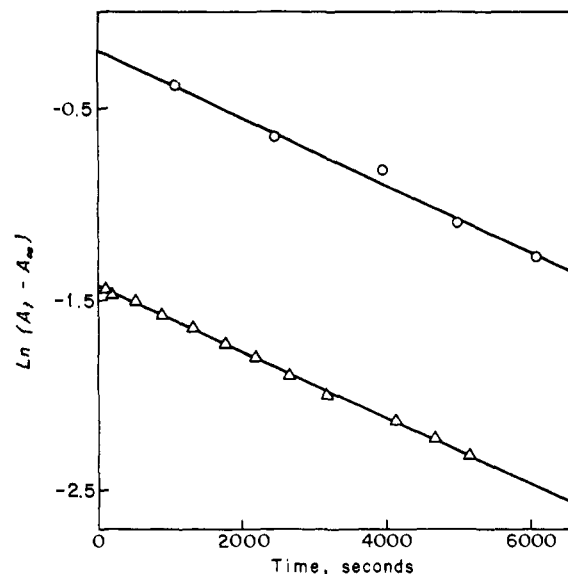
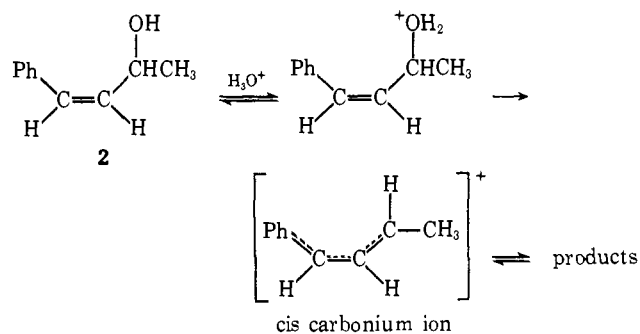
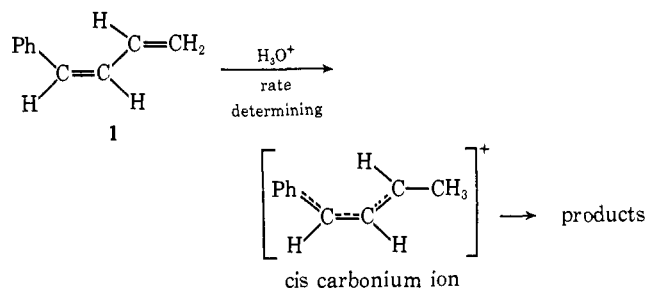


Figure 2. First-order plots of loss of  $^{18}\text{O}$  label from **2** (O) and isomerization of **2** ( $\Delta$ ) in 0.96 M perchloric acid in 40% aqueous dioxane solvent at 25°.

Turning to the isomerization of the cis-alkene **1**, this reaction is slower than the equilibration of the trans alcohol and trans alkene, so the product of this isomerization is the equilibrium mixture, and it is impossible to observe which is produced first. As in the case of the alcohol **2**, deuterium incorporation into the styryl



double bond is not observed, although the large rate retardation in deuterated media requires a rate-determining proton transfer to the substrate molecule.<sup>17</sup> Thus the only site available for protonation is the terminal carbon, and it is proposed that again the formation of the cis carbonium ion is rate determining.



The alternative mechanisms in eq 5 and 6 are both ruled out by the above considerations. Preequilibration with the alcohol is ruled out by the  $^{18}\text{O}$ -exchange experiment, since it would have to occur *via* the cis carbonium ion, which has been shown not to lead to

Table VII. Summary of Activation Parameters for Reactions Studied in Perchloric Acid-40% Aqueous Dioxane at 25°

Process	Estimated rel rate in 1 M acid	$\Delta H^\ddagger$	$\Delta S^\ddagger$
Rearrangement of <i>trans</i> -1-phenyl-3-methylallyl alcohol (3) <sup>a</sup>	1	18.2	-2.8 <sup>b</sup>
Racemization of <i>trans</i> -1-methyl-3-phenylallyl alcohol (4) <sup>a</sup>	$1.8 \times 10^{-2}$		
Isomerization of <i>cis</i> -1-methyl-3-phenylallyl alcohol (2)	$2.7 \times 10^{-3}$	23.0	+6 <sup>c</sup>
Dehydration of <i>trans</i> -1-methyl-3-phenylallyl alcohol (4) <sup>a</sup>	$4 \times 10^{-6}$	22.8	+0 <sup>c</sup>
Hydration of <i>trans</i> -1-phenyl-1,3-butadiene (5) <sup>a</sup>	$2.9 \times 10^{-5}$	18.7	-13 <sup>c</sup>
Isomerization of <i>cis</i> -1-phenyl-1,3-butadiene (1)	$6 \times 10^{-7}$	19.8	-19 <sup>c</sup>

<sup>a</sup> Data from ref 4. <sup>b</sup> At  $1.05 \times 10^{-3}$  M acid. <sup>c</sup> Calculated relative to the dehydration of 4.

*cis* alcohol. Thus the *cis* carbonium ion must isomerize faster than it reacts with water at the 3 position.

It was shown in our study of the rearrangement of 3<sup>4</sup> that the *trans* carbonium ion leads initially to the alcohol 4, so rotation of the C<sub>1</sub>-C<sub>2</sub> bond of the *cis* carbonium

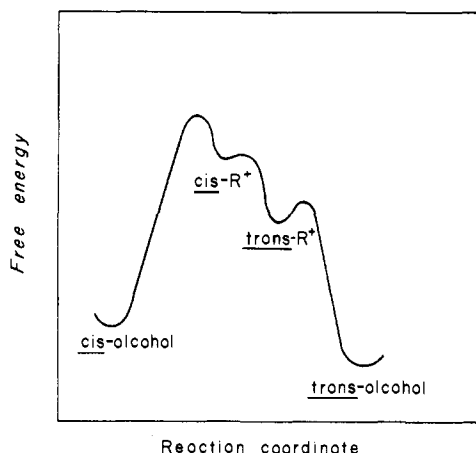
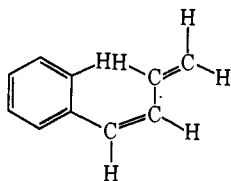


Figure 3. Free-energy diagram for the isomerization of 2, showing the *cis* and *trans* carbonium ions.

ion to yield the *trans* carbonium ion immediately on its formation meets all the requirements of the experimental observations. Objections to this may be raised on consideration of Young and Franklin's work discussed at the beginning of this paper, but the present case differs from theirs in one very important consideration. The *cis* alkene is known to be badly twisted out of plane by steric interactions between the hydrogen at the 3 position and an ortho hydrogen of the ring; estimates as



high as 52° for the angle between the plane of the ring and the side chain have been published.<sup>18</sup> This has the effect of lessening the conjugation between ring and side chain, with the result that the ultraviolet absorbance maximum is shifted 14 mμ to shorter wavelengths.

Naturally this interaction is also present in the *cis* carbonium ion, since its geometry is similar to that of the alkene, with the result that the π overlap along the side

chain is severely weakened. This π overlap provides the barrier to rotation about the C<sub>1</sub>-C<sub>2</sub> bond, so the conformational stability of this *cis* ion is much less relatively than that derived from *cis*-crotyl alcohol. Moreover, simple allylic cations such as the latter are known to collapse with solvent much faster than those with aromatic stabilization, so in the simple allylic compounds isomerization cannot compete with solvent attack.

One further alternative is that water attacks at C<sub>1</sub> giving the alcohol 3, which then gives the *trans* carbonium ion by rotation about the newly formed single bond, as in eq 2. However, it is hard to justify attack at the 1 position of the carbonium ion to the complete exclusion of attack at the 3 position, especially as the product 3 is so unstable in solutions of this acidity and the activated complex must partake of some of the character of the product. Similarly, one might avoid this argument altogether by postulating a concerted or intramolecular transfer of hydroxyl and generate 3 directly from 2, as was suggested by Braude,<sup>19</sup> but this type of mechanism for allylic alcohol rearrangements has been disproved many times<sup>4,6,20,21</sup> and need not be considered further. Thus the most reasonable mechanism remains the rate-determining formation of the *cis* carbonium ion followed by rapid rotation about its C<sub>1</sub>-C<sub>2</sub> bond prior to collapse with a water molecule of the solvent. This is the first case known of an allylic carbonium ion that is not stable with respect to *cis*-*trans* isomerization in aqueous solution. Whereas in the simple case the *cis* and *trans* compounds are of comparable free energies, in this instance they are not, as indicated in Figure 3.

It is of interest to compare the behavior of the *cis* alkene and alcohol with that of the *trans* system. In Table VII are listed the energies and entropies of activation for the reactions studied in this series of papers. It should be borne in mind that the relative rates shown are derived by extrapolation to a common acidity and this involves a certain amount of uncertainty. Nevertheless, several distinct trends are discernible.

The four fastest reactions involve alcohols. However, they tend to have rather higher activation energies than the reactions of the alkenes,<sup>22</sup> probably because the ground-state molecules are well solvated by hydrogen bonding to the hydroxyl group. This also accounts for the small entropies of activation, since the

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(21) W. Oroshnik, G. Karmas, and A. D. Mebane, *ibid.*, 74, 3807 (1952).

(22) Except for the rearrangement of 3, in which the substrate gains conjugation with the benzene ring, and therefore has a somewhat reduced activation energy.

(18) L. Zechmeister and A. L. LeRosen, *J. Amer. Chem. Soc.*, 64, 2755 (1942).

solvent shell is highly oriented in the ground state, and the rather specific solvation required for the activated complex in each case will not require too much reorganization of the solvent.

The two slowest reactions are rate-determining protonations of alkenes. In general, nonpolar molecules such as these are not specifically solvated in aqueous solution, but simply fit into cavities in the hydrogen-bonding matrix of the bulk solvent. To the extent that they interrupt the ordering of water molecules, they are destabilized relative to the pure alkene, in contrast to the alcohols, which gain hydrogen-bonding interactions on dissolving in water—hence the relatively smaller activation energies for the alkene reactions, since the transition state will be as highly solvated (and therefore solvent stabilized) as in the alcohol reactions. The entropies of activation also reflect this interpretation; since there is greatly increased ordering of solvent molecules in approaching the carbonium ion-like transition state, a fairly large negative entropy of activation is expected, and indeed observed. The differences between the entropies of activation for these two reactions are small, as would be expected of rate-deter-

mining generation of carbonium ions of the same geometric configuration as the starting material.

It is interesting that whereas in the trans system the carbonium ion is the intermediary in the equilibration between alkene and alcohol, in the cis system the corresponding carbonium ion acts as an interceptor, diverting the alkene and alcohol away from equilibration toward isomerization. Naturally, this is a consequence of the relative lifetimes of the two ions. The trans ion was shown<sup>4</sup> to be long lived enough that when generated from optically active **2** or **3** the optical activity was completely lost in the product. Likewise, if <sup>18</sup>O-labeled **2** or **3** were used, the <sup>18</sup>O-labeled water had time to diffuse out of the solvation sphere of the ion before collapse occurred. As has been amply shown here, the average lifetime of the cis ion must be very short indeed. This effect emphasizes once again the great importance to carbonium ion stability of conjugative dispersal of charge along an unsaturated system.

In conclusion, this system is a unique and very interesting one, showing that, even in the field of classical carbonium ions, experimental facts do not always fall along predictable lines.

## Benzocyclobutene Radical Anion<sup>1</sup>

Reuben D. Rieke,\* Steve E. Bales,<sup>2</sup> Phillip M. Hudnall, and Claude F. Meares<sup>3</sup>

Contribution from the Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514. Received June 29, 1970

**Abstract:** The radical anion of benzocyclobutene was prepared by metal and electrolytic reduction. Conclusive evidence is presented showing the fused, four-membered ring remains intact after reduction. An interesting temperature dependence was noted for the epr spectra of the metal-reduced benzocyclobutene. At low temperatures, the four methylene protons are nonequivalent but become equivalent as the temperature is raised. This phenomenon is discussed in terms of an ion pairing process. Finally, the effect of ring strain on spin densities and reduction potentials is discussed.

Since the original report of Mills and Nixon<sup>4</sup> more than 40 years ago, the study of the effects of ring strain on the chemical and physical properties of aromatic hydrocarbons has received considerable attention. Numerous reports have appeared concerning the increased preference for electrophilic attack  $\beta$  to the fused ring as strain is increased.<sup>5-9</sup> Markgraf,<sup>10</sup> *et al.*, have reported on the decrease in basicity of the lone

pair of electrons of a nitrogen atom  $\alpha$  to a fused ring as strain is introduced. Finnegan<sup>11</sup> and Streitwieser, *et al.*,<sup>12</sup> have reported on the increased acidity of the protons  $\alpha$  to the fused ring as strain is increased. Another observation<sup>13,14</sup> was the change in spin densities of radical anions of aromatic hydrocarbons with varying amounts of strain in the fused ring. Also, a large shift in half-wave reduction potential with strain has been noted.<sup>15,16</sup>

Several interpretations have been offered to explain these observations.<sup>12,17,18</sup> The argument presented by Streitwieser, *et al.*,<sup>12</sup> rests on a hybridization-polarization effect. This explanation, in contrast to the other

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- (17) J. Vaughan and G. J. Wright, *J. Org. Chem.*, **33**, 2580 (1968).
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