Reaction of 13 with Formic Acid. A. Product Study. A solution of 138 mg of en-yne **13** in 3.6 ml of formic acid (0.040 *M*) was heated at 70° for 12 hr. Water (20 ml) was added, and the mixture was extracted with two 10-ml portions of ether. The ethereal extracts were washed to neutrality with saturated sodium bicarbonate solution. After drying and removal of the ether by distillation and evaporation, a liquid weighing 140 mg (85% yield of ketone) remained. It showed a single major vpc peak with very small amounts of impurities. Its nmr, ir, and vpc retention time were almost identical with those of the commercial sample of 5-methyl-4-hexen-3-one (**9**).

B. Nmr Product Study. A solution of 58 mg (0.62 mmol) of **13** and 42 mg (0.62 mmol) of sodium formate in 0.80 ml of formic acid was prepared in an nmr tube and its spectrum was recorded at room temperature (see Figure 1C). This spectrum is similar to the spectrum of **13** in CCl_4 with single peaks at 1.37, 1.43, 1.52, and 1.55 ppm and a multiplet at 4.79 ppm from HMDS. Another sample prepared in the same way, was inserted in the variable-temperature probe at 70°. The first spectrum recorded at this temperature (see Figure 1D) shows single peaks at 1.20, 1.32, 1.40, and 1.46, a quartet of multiplets centered at 4.96, and a complex multiplet centered at 5.32 (two apparent maxima about 5 Hz apart) ppm from HMDS. Seven spectra were recorded in the first 3 hr, during which interval the conversion to **9** was less than half complete.

Preparation of 2,2-Dimethyl-1-pentyl Tosylate (16). To a cold solution of 18.0 g (0.095 mol) of *p*-toluenesulfonyl chloride in 200 ml of dry pyridine was added 10.0 g (0.86 mol) of 2,2-dimethyl-1-pentanol (Eastman practical grade). After the reaction mixture has been stirred for 12 hr, 600 ml of ice water was added. The mixture was extracted with two 150-ml portions of pentane–ether (1:1). The organic layers were extracted with two 100-ml portions of cold 5% sulfuric acid, 100 ml of saturated sodium bicarbonate solution, and 100 ml of water. After drying (sodium sulfate) and evaporation of the solvent, the remaining solvent and unreacted starting alcohol were removed by gently heating the residue for 4 hr *in vacuo* (1 mm). The liquid residue (19.5 g, 84%) was dissolved in 50 ml of pentane and cooled in a Dry Ice–acetone bath until crystals were formed. This recrystallization procedure was repeated seven times. The final liquid product was again taken up in pentane and dried and the solvent was thoroughly removed: weight 12.8 g; ir ($CHCl_3$), 1603 and 1475 (C_6H_4), 1360, 1190, and 1180 (SO_2), 1600, 965, and 850 cm^{-1}; nmr (CCl_4), δ 0.85 (singlet, $(CH_3)_2C$), a multiplet between 0.65 and 1.30 that overlaps the *gem*-dimethyl singlet (total area in this region is 13 H), 2.44 (3 H singlet, CH_3Ar), 3.59 (2 H singlet, CH_2O), 7.28 (2 H doublet, $J = 8$ Hz, ArH), and 7.72 (2 H doublet, $J = 8$ Hz, ArH).

Anal. Calcd for $C_{14}H_{22}SO_3$: C, 62.19; H, 8.20. Found: C, 62.41; H, 8.31.

Formolysis of 16. Nmr Kinetic Study. A solution of 77.1 mg (0.286 mmol) of **16** and 21.1 mg (0.21 mmol) of sodium formate in 0.60 ml of formic acid was prepared in an nmr tube. The reaction was followed at 75° by measuring the relative heights of the tosylate methyl peak at 2.11 ppm from HMDS and *p*-toluenesulfonic acid methyl peak at 2.05 ppm. Thirteen spectra were recorded over 10 hr.

Acknowledgments. Thanks are due to F. Marshall van Meter for preliminary work on this problem, to Daryl Sharp for obtaining the nmr spectra and to Dr. S. L. Smith, J. L. Alderfer, and H. E. Montgomery for help with the nmr work. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial financial support.

The Kinetics and Mechanism of the Acid-Catalyzed Rearrangement of 1-Phenyl-3-methylallyl Alcohol and the Hydration of 1-Phenyl-1,3-butadiene[1]

Y. Pocker[2] **and Martin J. Hill**

Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98105. Received December 21, 1968

Abstract: The kinetics of the acid-catalyzed rearrangement, racemization, and ^{18}O exchange of 1-phenyl-3-methylallyl alcohol (**1**) have been studied in 40% aqueous dioxane at 25.0°. The three reaction rates were found to be identical in a given acid solution, and were further shown to be proportional to the acid concentration with the same second-order rate constant, 6.8×10^{-2} l. mol^{-1} sec^{-1}. The kinetics of racemization and ^{18}O exchange of 3-phenyl-1-methylallyl alcohol (**2**) were also studied and the rates shown to be the same within experimental error, with second-order rate constant 1.2×10^{-3} l. mol^{-1} sec^{-1}. Finally, the rates of dehydration of **2** and hydration of 1-phenyl-1,3-butadiene (**3**) were followed and shown to correlate with the acidity of the medium, a plot of ln k *vs.* H_0 being linear with slope -1.49 in 40% dioxane and -1.22 in water. The mechanism of rearrangement of **1** thus involves protonation of **1** followed by unimolecular dissociation of the protonated species to form the intermediate carbonium ion, which is partitioned almost exclusively in favor of **2**. The hydration of **3** proceeds *via* a rate-determining protonation of **3** to form the same carbonium ion, and the rate of the dehydration of **2** is governed by the corresponding deprotonation of the carbonium ion.

The phenomenon of carbonium ion return is well documented in the rearrangement of allylic esters.[3a,b] The detection of return depends on the measurement of the rates of racemization, exchange, and rearrangement of the ester. For example, in the acetolysis of 1-phenylallyl acetate the rate of rearrangement to form cinnamyl acetate provides a minimum rate of ionization. However, both the racemization and ^{14}C-exchange rates are faster, indicating that the initially

---

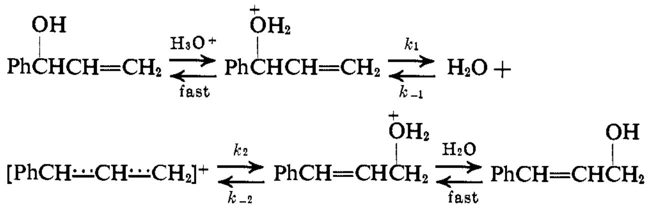
(1) Supported in part by grants from the National Science Foundation (NSF GP-5103) and the Petrolenm Research Fund (PRF 2043-A4) administered by the American Chemical Society. Grateful acknowledgment is made to the donors of these funds.

(2) To whom inquiries should be directed.

(3) (a) Y. Pocker, *J. Chem. Soc.*, 4318, 4323 (1958); (b) Y. Pocker, *Proc. Chem. Soc.*, 226 (1959); (c) Y. Pocker and M. H. Andrus, Jr., unpublished observations; M. H. Andrus, Jr., Ph.D. Thesis, University of Washington, 1967.

formed carbonium ion returns to starting material at a rate comparable to that of product formation.[3b,c]

Similarly, in 1958 two groups[4–7] simultaneously investigated the mechanism of the acid-catalyzed rearrangement of 1-phenylallyl alcohol in aqueous dioxane solvent. Both groups obtained essentially the same results, namely that as in the acetate case the rates of racemization and ^{18}O exchange from 1-phenylallyl alcohol are faster than the rate of rearrangement by a factor of *ca.* 1.6, again showing that return is competitive with product formation.



$$\mathrm{Ph\overset{OH}{C}HCH{=}CH_2} \underset{\text{fast}}{\overset{\mathrm{H_3O^+}}{\rightleftarrows}} \mathrm{Ph\overset{\overset{+}{O}H_2}{C}HCH{=}CH_2} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{H_2O} +$$

$$[\mathrm{PhCH{\cdots}CH{\cdots}CH_2}]^+ \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{PhCH{=}CH\overset{\overset{+}{O}H_2}{C}H_2} \underset{\text{fast}}{\overset{\mathrm{H_2O}}{\rightleftarrows}} \mathrm{PhCH{=}CH\overset{OH}{C}H_2}$$

$$\frac{k_{-1}}{k_2} = \frac{23.3}{14.2} = 1.6$$

In their second paper, Goering and Dilgren[7] indicated the presence of a small component of the reaction, *ca.* 8%, proceeding by an apparently intramolecular rearrangement. The experiments starting with 1-phenylallyl alcohol-^{18}O in water of normal isotopic abundance produce, according to these authors, a small but detectable amount of cinnamyl alcohol-^{18}O. Since the cinnamyl alcohol molecule has no asymmetry, the rearrangement necessarily proceeds with complete racemization, and studies of the loss of optical activity from 1-phenylallyl alcohol cannot be used to scrutinize this finding. The present paper contains reports on the rearrangement of 1-phenyl-3-methylallyl alcohol (**1**), carried out with the expectation that any intramolecular transfer of hydroxyl to the product 3-phenyl-1-methylallyl alcohol (**2**) would be accompanied by some retention of optical activity.

During the course of this work it was found that the racemization of **2** was accompanied by the production of a third material subsequently shown to be 1-phenyl-1,3-butadiene (**3**). Since it appeared reasonable that the dehydration of **2** would lead to **3** *via* the same intermediate carbonium ion as the rearrangement of **1**, the kinetics of both this process and the hydration of **3** were studied also.

Experimental Section[8]

Preparation of Materials. ***dl*-1-Phenyl-3-methylallyl Alcohol (1).** To 24 g of magnesium and 300 ml of dry THF was added a solution of 1 mol of bromobenzene in 200 ml of dry THF at such a rate as to keep the THF refluxing. Refluxing was continued by means of a steam bath for 1 hr after addition, and the flask was cooled to 5° in an ice bath. A solution of 1 mol of crotonaldehyde in 100 ml of the THF was dropped in with stirring, maintaining the temperature below 10°, and the mixture left overnight. The mixture was slowly added to 50 ml of ice water and filtered, the volume reduced on a rotary evaporator and extracted with ether, the ether layer dried over calcium sulfate, the ether evaporated, and 1-phenyl-3-methylallyl alcohol distilled, bp 90–92° (2 mm).

(−)-1-Phenyl-3-methylallyl alcohol was prepared by a modification the method of Kenyon, Partridge, and Phillips.[9] A 40-g sample of **1** and 40 g of phthalic anhydride were heated in 60 g of pyridine for 2 hr at 35–40°. On cooling the mixture was stirred with ice water and the oily residue separated. The phthalate ester was crystallized from ether–petroleum ether (bp 30–60°) yielding 70 g of material, mp 93–94°. To a hot solution of 40 g of phthalate in 200 ml of freshly distilled methyl acetate were added 40 g of quinidine, and the mixture was stirred on the steam bath until the quinidine dissolved. On cooling, a massive white precipitate of the partially resolved quinidine salt was obtained. The precipitate was filtered off, dried, and recrystallized from 2300 ml of methyl acetate, mp 135–136°, yield 17.2 g. The quinidine salt was added to 100 ml of a 5 *M* sodium hydroxide solution in 95% ethanol and the mixture heated to boiling. On steam distillation (−)-1-phenyl-3-methylallyl alcohol was obtained, and was extracted with ether, dried over calcium sulfate, and distilled, bp 92–94° (3–4 mm), yield 4 g, $[\alpha]^{25}_{5461}$ 21.0°.

1-Phenyl-3-methylallyl Alcohol-^{18}O. To 10 ml of freshly distilled crotonaldehyde were added 17 ml of ^{18}O enriched water (1.4 atoms % excess) and a catalytic amount of *p*-toluenesulfonic acid, and the mixture stirred for 48 hr at room temperature. The resulting crotonaldehyde-^{18}O was extracted with ether and the solution dried over calcium sulfate. A Grignard reaction as above was used to prepare 1-phenyl-3-methylallyl alcohol-^{18}O, bp 83° (1.8 mm), yield 18 g.

***dl*-3-Phenyl-1-methylallyl alcohol (2) and (+)-3-phenyl-1-methylallyl alcohol** were prepared by the method of Kenyon, Partridge, and Phillips.[10]

3-Phenyl-1-methylallyl Alcohol-^{18}O. To 20 g of freshly distilled *trans*-4-phenyl-3-buten-2-one were added 25 ml of ^{18}O-enriched water (1.0 atom % excess) and a catalytic amount of *p*-toluenesulfonic acid, 5 ml of THF were added to increase the solubility of the ketone, and the mixture was stirred at room temperature for 2 days. The resulting labeled ketone was extracted with ether and dried over calcium sulfate. The ketone was dissolved in 100 ml of 95% aqueous ethanol, and a solution of 2.0 g of sodium borohydride in 2 ml of 2 *M* sodium hydroxide diluted to 20 ml with water was added, with cooling to keep the temperature below 25°, and the mixture was added, with cooling to keep the temperature below 25°, and the mixture was allowed to stand for 1 hr. The volume was reduced on a rotary evaporator and the mixture extracted with ether, the extracts dried over calcium sulfate, filtered, and distilled, yielding 3-phenyl-1-methylallyl alcohol-^{18}O, bp 94–96° (1.1 mm), and 0.798 atom % excess. At 252 mμ the extinction coefficient of this material was 16,300, showing that none of it had been reduced to 4-phenyl-2-butanol.

1-Phenyl-1,3-butadiene (3) was prepared by the method of Muskat and Herman.[11] **1,4-Dioxane** was purified as described in Vogel[12] and distilled through a 4-ft column packed with glass helices until its absorbance at 252 mμ was less than 0.300 with respect to distilled water. The 40% dioxane solvent was made up by pipetting 400 ml of dioxane into a 1-l. volumetric flask and making the solution up to the mark with distilled, deionized water, care being taken to keep the temperature at 20°. Acid solutions were made by weighing quantities of 71% aqueous perchloric acid into a 1-l. flask, pipetting in enough dioxane to make up the water present up to 40% dioxane by volume, and making up to the mark with 40% dioxane solvent, again maintaining the temperature at 20°. The acid concentrations for all runs but exchange runs were checked by titration against standard sodium hydroxide solutions. For the various exchange runs the acid concentrations were checked by carrying out rearrangement runs in the same solutions.

Kinetic Methods. The rearrangement of **1**, the dehydration of **2**, and the hydration of **3** were followed spectrophotometrically for two to three half-lives using a Beckman Model DU spectrophotometer fitted with a specially constructed thermostated cell compartment controlled by a Sargent Thermonitor to a temperature of 25.00 ± 0.05°. The rearrangement was followed at 252 mμ where the molar absorptivity of **1** is $\epsilon \simeq 200$ and of **2** is $\epsilon \simeq 16800$, and the hydration and dehydration were followed at 280 mμ where **2** has

---

(4) C. A. Bunton, Y. Pocker, and H. Dahn, *Chem. Ind.* (London), 1516 (1958).

(5) Y. Pocker, *ibid.*, 195 (1959).

(6) H. L. Goering and R. E. Dilgren, *J. Amer. Chem. Soc.*, **81**, 2556 (1959).

(7) H. L. Goering and R. E. Dilgren, *ibid.*, 82, 5744 (1960).

(8) Melting points and boiling points are uncorrected. Ultraviolet spectra were determined using a Cary Model 14 spectrophotometer.

(9) J. Kenyon, S. M. Partridge, and H. Phillips, *J. Chem. Soc.*, 207, (1937).

(10) J. Kenyon, S. M. Partridge, and H. Phillips, *ibid.*, 85 (1936).

(11) I. E. Muskat and M. Herman, *J. Amer. Chem. Soc.*, **53**, 252 (1931).

(12) A. I. Vogel, "A Textbook of Practical Organic Chemistry including Qualitative Organic Analysis," 3rd ed, John Wiley & Sons, Inc., New York, N. Y., 1966, p 177.

Table I. Rearrangement of 1-Phenyl-3-methylallyl Alcohol at 25°

$[HClO_4]$, 10^3 M	10^4k, sec^{-1}	$10^2k' = k/[HClO_4]$, l. mol^{-1} sec^{-1}
	a. Spectrophotometric Rates	
1.47	1.00	6.80
2.80	1.98	7.09
4.74	3.13	6.60
7.8	5.31	6.78
8.2	5.73	6.82
14.7	9.8	6.71
19.0	13.0	6.85
23.7	16.2	6.84
		Mean $k' = (6.81 \pm 0.09)10^{-2}$
	b. Polarimetric Rates	
1.47	0.996	6.77
2.8	1.79	6.39
4.8	3.40	7.08
7.0	4.77	6.81
8.4	6.20	7.38
9.8	6.56	6.69
10.0	6.81	6.81
12.0	8.03	6.69
12.2	8.57	7.00
		Mean $k' = (6.84 \pm 0.2)10^{-2}$

c. ^{18}O-Exchange Rates

$[HClO_4]$, 10^3M	10^4k_{rearr}, sec^{-1}	10^4k_{ex}, sec^{-1}	k_{ex}/k_{rearr}
1.56	1.06	1.06	1.00
3.16	2.15	2.20	1.02
16.7	11.4	11.4	1.00

Table II. Activation Energy Data

a. Rearrangement of 1-Phenyl-3-methylallyl Alcohol

$HClO_4$, 10^3 M	Temp, °C	10^4k, sec^{-1}
2.57	10.00	0.71
	15.00	1.29
	25.00	3.77
	35.00	10.4
1.05	10.00	2.87
	15.00	5.2
	25.00	15.4
	25.00	39.3
4.11	10.00	1.14
	15.00	2.07
	25.00	6.02
	35.00	16.7

b. Hydration of 1-Phenyl-1,3-butadiene and Dehydration of 3-Phenyl-1-methylallyl Alcohol

Acid, M	Temp, °C	10^3k, sec^{-1}	% $\mathbf{2}_{eq}$	10^3k_{hyd}, sec^{-1}	10^3k_{deh}, sec^{-1}
		(i) Aqueous H_2SO_4			
3.91	20.00	1.32	84	1.11	0.21
	25.00	2.08	81	1.68	0.40
	35.00	7.2	77	5.5	1.66
	40.00	12.2	75	8.4	2.8
3.14	20.00	0.42	86	0.36	0.055
	25.00	0.77	84	0.65	0.124
	35.00	2.50	81	2.05	0.47
	40.00	4.30	79	3.41	0.90
		(ii) $HClO_4$ in 40% Aqueous Dioxane			
2.92	15.00	0.118	60	0.071	0.047
	25.00	0.394	55	0.217	0.177
	35.00	1.30	49	0.64	0.66
3.37	15.00	0.311	61	0.190	0.121
	25.00	1.10	57	0.63	0.47
	35.00	3.40	50	1.70	1.70

Table III. Racemization and Exchange Rates of 3-Phenyl-1-methylallyl Alcohol

$[HClO_4]$, M	10^4k, sec^{-1}	$k' = k/[HClO_4]$, l. mol^{-1} sec^{-1}
	a. Racemization	
0.0225	0.24	1.07×10^{-3}
0.108	1.29	1.19×10^{-3}
0.180	2.18	1.21×10^{-3}
0.217	2.41	1.11×10^{-3}
0.271	3.45	1.27×10^{-3}
0.333	4.60	1.39×10^{-3}
		Mean $k' = (1.21 \pm 0.08)10^{-3}$
	b. ^{18}O Exchange	
0.0167	0.197	1.18×10^{-3}

$\epsilon \simeq 1250$ and **3** has $\epsilon \simeq 28{,}300$. In each case 3 ml of acid solution were pipetted into each cell and allowed to reach thermal equilibrium. A 0.05-ml sample of a standard substrate solution was introduced by means of a tuberculin syringe, and the cell shaken to ensure intimate mixing of the solutions before introduction into the DU. The resulting dilution was taken into account when the acid concentrations were calculated. Pseudo-first-order rate constants were calculated from plots of ln $(A_\infty - A_t)$ *vs.* time and are tabulated in Tables I, II, and IV.

The loss of optical activity of **1** and **2** was followed using a Bendix Automatic Digital Polarimeter, Model 953. The cells were contained in water jackets connected to a thermostat and were pre-equilibrated at 25°. A quantity of substrate was weighed out in a 10-ml flask, sufficient acid to fill the cell was added, the flask shaken vigorously and the solution poured into the cell. The rotation at ten half-lives was used for α_∞ in the racemization of **1**. In the case of **2**, the solution became cloudy after about two half-lives, and small bubbles of **3** separated before ten half-lives, so a real α_∞ value was not obtainable. An initial reading of the rotation of the acid solution minus substrate was used instead, and gave straight line plots through one half-life. Pseudo-first-order rate constants were calculated from plots of ln $(\alpha - \alpha_\infty)$ *vs.* time, and are listed in Tables I and III.

The loss of ^{18}O-label from labeled **1** and **2** were followed by dissolving 4–4.5 g of substrate in 800 ml of acid solution maintained at 25.0° in a water bath, and withdrawing and quenching 100-ml aliquots at specific times. After quenching with potassium carbonate, each aliquot was saturated with sodium chloride and extracted with ether. The extracts were dried over sodium sulfate, filtered, and divided into three parts, each of which was dried over calcium sulfate and filtered, and the ether and dioxane evaporated. The remaining mixtures of **1** and **2** were sealed into glass tubes of capacity about 2 ml containing 1 μl of concentrated sulfuric acid and an atmosphere of carbon dioxide. The tubes were heated at 150° for 24 hr, after which time the oxygens of the mixture of **1** and **2** were equilibrated with those of the carbon dioxide. The ratio of mass 44 to mass 46 carbon dioxide was measured on a Consolidated Engineering Mass Spectrometer Model 21-103 modified so as to scan these peaks alternately and display them on an oscilloscope. The amount of attenuation of the high abundance peak necessary to make the two peak heights equal gave the ratio of isotopic abundances. Alternation of these samples with samples of natural carbon dioxide demonstrated the high precision of this method, which is derived from those of Anbar, *et al.*,[13] and Pocker and Gray.[14]

Results

The results of kinetic experiments on the rearrangement are summarized in Table I. The extinction coefficient of **2** produced during the course of the kinetic runs was found to coincide exactly with that of an independently synthesized sample ($\epsilon \simeq 16800$ at 252 mμ), indicating that within experimental error (*ca.* 1%) the rearrangement proceeds to completion. Braude, *et al.*,[15] however, found that the product of

---

[13] M. Anbar, I. Dostrovsky, F. Klein, and D. Samuel, *J. Chem. Soc.*, 155 (1955).

[14] Y. Pocker and J. P. Gray, unpublished observations; J. P. Gray, Ph.D. Thesis, University of Washington, 1968.

[15] E. A. Braude, E. R. H. Jones, and E. S. Stern, *J. Chem. Soc.*, 396 (1946).

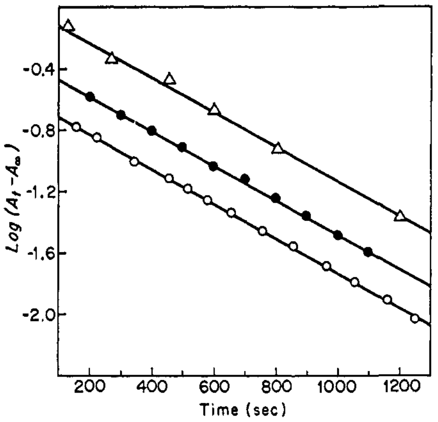


Figure 1. First-order plots of rearrangement of 1-phenyl-3-methylallyl alcohol (○), loss of optical activity of (−)-1-phenyl-3-methylallyl alcohol (●), and loss of ^{18}O label from 1-phenyl-3-methylallyl alcohol-^{18}O (△) in 1.66×10^{-2} M $HClO_4$ in 40% dioxane solvent at 25.0°.

rearrangement had an absorptivity *ca.* 8% less than their independently synthesized product. Since they did not have the advantage of vapor phase chromatography it is quite possible that the discrepancy between their result and the present one is due to impurities in their materials. The infinity absorbance values were shown to be stable for at least ten half-lives for rearrangement, corroborating the conclusion that under these conditions significant side reactions are absent. Rearrangement runs gave good pseudo-first-order kinetics through at least three half-lives, as shown in Figure 1. It is clear from the proportionality of pseudo-first-order rate constants to acid concentration shown in Table I that the rearrangement is second order over-all, and first order with respect to acid and substrate. Plots of ln k *vs.* $1/T$ gave straight lines of mean slope 9460°K, and hence the activation energy, E_a, was calculated to be 18.8 kcal/mol. The free energy of activation, ΔF^*, the enthalpy of activation, ΔH^*, and the entropy of activation, ΔS^*, were calculated to be 19.05 kcal/mol, 18.2 kcal/mol, and −2.8 eu, respectively.

The loss of optical activity of partially resolved **1** was followed through 60% reaction and also gave good pseudo-first-order kinetics (Table I, part b). The product **2** was found to have no detectable optical activity at ten half-lives of loss of optical activity of **1**, indicating that the rearrangement proceeds with complete racemization of **1**. It is worthy of note that the rate constants for rearrangement and racemization are the same within experimental error.

The racemization of partially resolved **2** was shown to be *ca.* 56 times slower than the loss of optical activity of **1**, so it may be safely concluded that **1** loses its optical activity during rearrangement, and that the racemization of **1** is similarly slow.

To complete the study of the rearrangement, the kinetics of the loss of ^{18}O label from labeled **1** and **2** were followed, with results as shown in Tables I and III. Again, the rate of loss of label from **1** is equal to the rate of rearrangement, and that from **2** is relatively slow, indicating that loss of label occurs during rearrangement. The residual label in **2** arising from rearrangement of **2** was very small and equal to the ^{18}O-excess of the solvent water at the end of the reaction. An aliquot quenched at 50% reaction and whose components were separated by vapor phase chromatography (column: 7% STAP on 70–80 Varaport No. 30) consisted of **1** retaining about 10% less than the original percentage of label, and **2** that had about 10% more label than the infinity value. However, it was later shown that **1** undergoes thermal rearrangement and exchange on the column, so it is reasonable to conclude that the rearrangement product does not contain a significant quantity of ^{18}O-label.

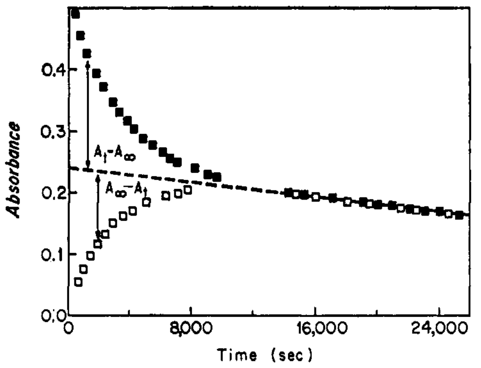


Figure 2. Plot of absorbance *vs.* time for dehydration of 3-phenyl-1-methylallyl alcohol (□) and hydration of 1-phenyl-1,3-butadiene (■) in 2.9 M $HClO_4$ in 40% dioxane solvent at 25.0°.

The results of the kinetic study of the dehydration of **2** and the hydration of **3** are summarized in Tables II and IV. In 40% dioxane solvent both reactions proceeded to an equilibrium consisting of 50–60% **2**. The infinity values were observed to decrease with time due to a side reaction apparently first order with respect to acid and substrate, and thus this side reaction is most likely to involve hydration of the styryl double bond of **2**. The infinity values used to calculate the rate constants were obtained by extrapolating back to zero time as indicated in Figure 2. Using these values, kinetic runs originating from either **2** or **3** as starting

Table IV. Dehydration of 3-Phenyl-1-methylallyl Alcohol and Hydration of 1-Phenyl-1,3-butadiene at 25°

Acid, M	10^4k_{obsd} (**3**), sec^{-1}	10^4k_{obsd} (**2**), sec^{-1}	$-H_0$	Log k_{obsd} (**3**) + H_0	Log k_{obsd} (**2**) + H_0	% **2**$_{eq}$
			a. Aqueous H_2SO_4			
2.33	2.32	2.44	1.05	−4.70	−4.66	83
3.14	7.8	7.6	1.45	−4.56	−4.57	84
3.23		8.5	1.50		−4.57	
3.76	16.1		1.76	−4.55		
3.91	20.7	20.8	1.82	−4.50	−4.50	81
4.27	30.8	31.8	1.97	−4.48	−4.46	82
			b. $HClO_4$ in 40% Aqueous Dioxane			
2.50		1.71	0.63		−4.40	
2.62	2.02		0.71	−4.40		
2.78		2.99	0.81		−4.33	54
2.88		3.77	0.88		−4.30	55
2.91	3.94	4.28	0.90	−4.30	−4.27	57
3.13		6.07	1.04		−4.26	57
3.29		9.3	1.15		−4.18	
3.37	10.9	11.1	1.20	−4.16	−4.15	57
3.45	12.9		1.25	−4.14		
3.70		24.6	1.41		−4.02	60
3.89	37.0		1.54	−3.97		61
4.12		63.5	1.69		−3.89	62
4.35	71		1.74	−3.89		

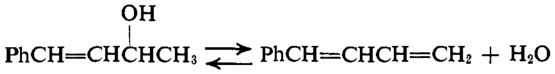
materials gave good pseudo-first-order kinetics for two half-lives. The rate constants yielded a good straight line of slope 1.49 in a plot of log k *vs.* H_0.[16] The values of the equilibrium in Table IV were calculated from the observed absorptions of the equilibrium mixture at 252 and 280 mμ (A_{252} and A_{280}), at which wavelengths the extinction coefficients of **2** are ϵ_{252} 16,800 and ϵ_{280} 1250 and of **3** are ϵ_{252} 10,600 and ϵ_{280} 28,300, and by solving the following simultaneous equations

$$C_2(16{,}800) + C_3(10{,}600) = A_{252}$$

$$C_2(1250) + C_3(28{,}300) = A_{280}$$

where C_2 and C_3 represent the concentrations of **2** and **3**, respectively. The values obtained using **2** as starting material agreed within ±2% with those derived from **3**, showing that the two reactions do indeed proceed to the same equilibrium position.

Since for the reaction



$$\mathrm{PhCH{=}CH\overset{\displaystyle OH}{\overset{|}{C}}HCH_3} \rightleftharpoons \mathrm{PhCH{=}CHCH{=}CH_2 + H_2O}$$

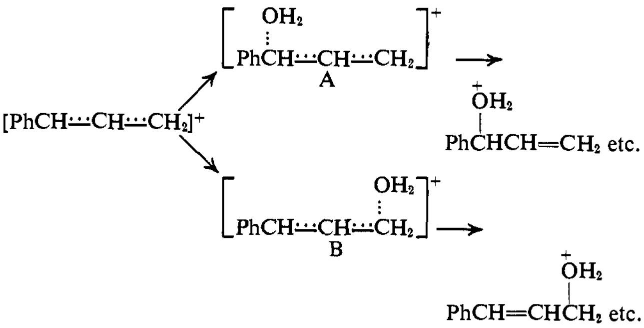
$k_{obsd} = k_{hyd} + k_{deh}$ and $K_{eq} = k_{hyd}/k_{deh} = \%\,\mathbf{2}_{eq}/\%\,\mathbf{3}_{eq}$, values for k_{hyd} and k_{deh} were calculated. Using values obtained in this manner, plots of ln k_{deh} and ln k_{hyd} *vs.* $1/T$ were found to give straight lines of slope 11,800°K and 9730°K, respectively, and hence activation energies of 23.4 and 19.3 kcal/mol for the dehydration of **2** and the hydration of **3**.

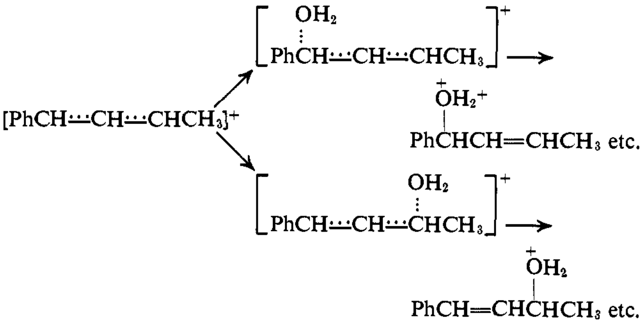
The kinetic data obtained in aqueous sulfuric acid were treated in a similar manner, and the results are shown in Tables II and IV. Again the infinity values showed some decrease with time, but at a greatly reduced rate compared to those obtained in 40% dioxane. Both hydration and dehydration gave good pseudo-first-order kinetics through two half-lives, and again a plot of log k *vs.* H_0[17] gave a straight line, in this case of slope 1.22. Plots of ln k_{deh} and ln k_{hyd} gave straight lines of slope 12,400°K and 10,500°K, and the activation energies of dehydration of **2** and hydration of **3** were calculated to be 24.6 and 20.9 kcal/mol.

Discussion

Considering the rearrangement first, it will be noted from Figure 1 especially that the rates of loss of optical activity and loss of ^{18}O label from **1** are equal to the rate of rearrangement. Since the product **2** retains neither optical activity nor label there can be no intramolecular component to the reaction. Thus the mechanism must involve a simple heterolysis of protonated **1** to yield an intermediate carbonium ion whose lifetime is long enough to ensure complete loss of asymmetry and complete loss of the departing water molecule to the surrounding solvent. Furthermore, the equality of all three rates requires that the carbonium ion, once formed, does not return to starting material at all, but proceeds completely to product. Thus the rate-determining step is the formation of the carbonium ion rather than the formation of product (in the case of 1-phenylallyl alcohol the partitioning of the carbonium ion is about 60% in favor of return to starting material, so the rate-limiting step is the further reaction of the carbonium ion yielding product).

The change of mechanism on adding a terminal methyl group to 1-phenylallyl alcohol can be rationalized by a consideration of the two transition states possible in each case.





For the 1-phenylallyl case, transition state A stabilizes the partial positive charge by distribution of the charge around the ring and by induction by virtue of its position at a secondary carbon. Transition state B, however, has its major concentration of charge at a primary carbon, and this tends to offset the large stabilization arising from the styryl conjugation. The net result is that the free energies of the two transition states are nearly equal, so that return competes with product formation.

In the present case, both possible sites for attack are secondary carbons, and the transition state with styryl conjugation is significantly more stable than that with phenyl stabilization. It is interesting to note that here not only do small changes in transition-state energies cause relatively large changes in over-all reaction rates, but the balance of the rates of the component processes is altered decisively by the mere substitution of hydrogen for methyl.

Since formation of **3** during rearrangement was not detected, and since the rates of racemization and ^{18}O exchange from **2** are considerably faster than the rate of formation of **3** from **2**, the transition state leading to **3** from the intermediate carbonium ion must be greatly higher in free energy than that leading to **2**. Thus the rate-determining step in the dehydration of **2** is the extraction of a proton from the carbonium ion, and that in the hydration of **3** is the donation of a proton to **3** by a hydronium ion. The interpolation of an additional step involving the formation of a π complex of the olefin with a proton in the manner of Taft,[18] for example, is not excluded, but is, in the opinion of the authors, not necessary. Similar conclusions have been

---

(16) H_0 values were obtained from C. A. Bunton, J. B. Ley, A. J. Rhind-Tutt, and C. A. Vernon, *J. Chem. Soc.*, 2327 (1957).

(17) H_0 values were obtained from M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

(18) R. H. Boyd, R. S. Taft, Jr., A. P. Wolf, and D. R. Christman, *J. Amer. Chem. Soc.*, **82**, 4729 (1960).

reached in the study of the hydration of styrene[19,20] and stilbene.[21]

The linearity of the plots of log k *vs.* H_0 is not significant of itself, as H_0 is approximately proportional to the acid concentration over these ranges of acidity,[16,17] and so log k is also approximately proportional to the log of the acid concentration. Thus the presence or absence of a water molecule in the transition state is a moot point. However, the observed slopes of 1.22 in water and 1.49 in 40% dioxane agree nicely with the suggestion that higher slopes correspond to transition states more weakly solvated by water,[18–21] since there is clearly less water available for solvation in the mixed solvent.

It is proposed to further this research by undertaking a parallel study on the rearrangement of 1-phenyl-3-(trideuteriomethyl)allyl alcohol and the dehydration of 3-phenyl-1-(trideuteriomethyl)allyl alcohol and the hydration of 1-phenyl-4,4-dideuterio-1,3-butadiene.

---

[19] Y. Pocker and A. E. Miller, unpublished results; A. E. Miller, Ph.D. Thesis, University of Washington, 1968.

[20] W. M. Schubert, B. Lamm, and J. R. Keefe, *J. Amer. Chem. Soc.*, **86**, 4727 (1964); W. M. Schubert and B. Lamm, *ibid.*, **88**, 120 (1966).

[21] D. S. Noyce, D. R. Hartter, and F. B. Miles, *J. Amer. Chem. Soc.*, 90, 4633 (1968).

Hydroxyl Proton Magnetic Resonance Study of Aliphatic Alcohols[1a]

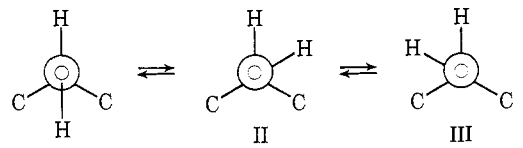
Charles P. Rader[1b]

Contribution from the Organic Chemicals Division, Monsanto Co.,
St. Louis, Missouri 63177. *Received January 9, 1969*

Abstract: The constancy of the hydroxyl–carbinol proton coupling constant (J_{HCOH}) for rotamerically homogeneous methanol in hydrogen-bonding media indicates that J_{HCOH} variations for different alcohols in these media may be attributed to conformational changes. J_{HCOH} measurements for sterically unhindered primary alcohols suggest that the three C–O bond rotamers are approximately equally populated. Similar measurements for unhindered secondary alcohols suggest the rotamer with the OH staggered between the two C–C bonds to be significantly less populated than the other two. For both primary and secondary alcohols substitution of alkyl groups on a carbon β to the OH consistently increases J_{HCOH}. This is attributed to a slight but significant decrease in the equilibrium H–C–O–H dihedral angle of some of the C–O bond rotamers in which the OH is staggered between a C–H and a C–C bond. For secondary cyclic alcohols in which the hydroxyl hydrogen is constrained to be only *gauche* or *anti* to the carbinol hydrogen, J_{HCOH} values reveal the simplified Karplus relation ($J_{\mathrm{HCOH}} = A \cos^2 \phi$) to be followed to a good approximation. In dimethyl sulfoxide the hydroxyl proton chemical shift, relative to that of the neat alcohol, can be correlated with the degree of steric crowding around the OH group.

Methods for the facile observation of spin–spin coupling between the hydroxyl and other protons of alcohols are now well known.[2] As a result, the recent literature reports a number of studies involving vicinal[3] and long-range[4] coupling of the hydroxyl proton. The preponderance of these studies have been carried out in polar solvents which can donate an electron pair to form a hydrogen bond with the O–H proton and thus decrease its rate of exchange. The observation of this coupling in nonpolar solvents requires that greater attention be given to both solvent and solute purity.

Much experimental evidence may now be found for the existence, at least in a qualitative sense, of a Karplus type relation[5] between the H–C–O–H coupling constant (J_{HCOH}) and the corresponding dihedral angle. A previous study in these laboratories[6] and a similar one by Uebel and Goodwin[7] have shown that for a pair of epimeric cyclohexanols J_{HCOH} is greater for the equatorial epimer due to the existence of a significant population of the *anti* rotamer (I) of this epimer, whereas, for the axial epimer steric considerations require that this conformer have a population much less than that of II or III. Other researchers have reported[8–10] cases where J_{HCOH} is unusually large due to the OH existing primarily, if not entirely, in the *anti* conformation (I) as a result of intramolecular hydrogen bonding. These and other studies indicate that hy-


I II III

---

[1] (a) Presented in part at the Midwest Regional Meeting, American Chemical Society, Manhattan, Kan., Nov 1, 1968; (b) address inquiries to the Monsanto Co., Akron, Ohio 44313.

[2] (a) P. L. Corio, R. L. Rutledge, and J. R. Zimmerman, *J. Am. Chem. Soc.*, **80**, 3163 (1963); (b) O. L. Chapman and R. W. King, *ibid.*, 86, 1256 (1964); (c) J. M. Bruce and P. Knowles, *J. Chem. Soc.*, 5900 (1964); (d) E. Krakower and L. W. Reeves, *Trans. Faraday Soc.*, **59**, 2528 (1963).

[3] (a) W. B. Moniz, C. F. Poranski, Jr., and T. N. Hall, *J. Am. Chem. Soc.*, **88**, 190 (1966); (b) J. G. Traynham and G. A. Knesel, *ibid.*, **87**, 4220 (1965); (c) B. Casu, M. Reggiani, G. G. Gallo, and A. Vigevani, *Tetrahedron Letters*, 2253 (1965).

[4] J. C. Jochims, G. Taigel, A. Seeliger, P. Lutz, and H. E. Driesen, *ibid.*, 4363 (1967).

[5] M. Karplus, *J. Chem. Phys.*, 30, 11 (1959); (b) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).

[6] C. P. Rader, *ibid.*, **88**, 1713 (1966).

[7] J. J. Uebel and H. W. Goodwin, *J. Org. Chem.*, **31**, 2040 (1966).

[8] N. L. Bauld and Y. S. Rim, *ibid.*, **33**, 1303 (1968).

[9] A. L. Ternay, Jr., and D. W. Chasar, *ibid.*, **33**, 2237 (1968).

[10] R. D. Stolow and A. A. Gallo, *Tetrahedron Letters*, 3331 (1968).