ancy recorded in one of the parameters. Moreover, the fact that carbonato-apatite differs from hydroxy-apatite because of the replacement of hydroxyls by carbonate ions is evidenced by the information obtained by means of infrared spectroscopy.

Kinetics and Mechanism of the Pinacol Rearrangement. I. The Perchloric Acid-catalyzed Rearrangement of Benzopinacol and of Tetraphenylethylene Oxide in Acetic Acid Solution[1]

By Herbert J. Gebhart, Jr.,[2] and Kenneth H. Adams

The perchloric acid-catalyzed rearrangement of benzopinacol (P) to β-benzopinacolone (K) in acetic acid occurs by two kinetically distinguishable routes, one of which involves direct rearrangement and the other involves intermediate formation of tetraphenylethylene oxide (E). At 75° approximately 80% of the ketone is formed by the latter route. Correlation of H_0 values of the medium with the rate constants of the reaction system P → E → K shows that for the three reactions a reversible proton transfer to P or E is followed by the rate-determining ionization of the oxonium complex. The large positive values of the entropy of activation for the rearrangement of E and for the composite reaction of P suggest that the classical carbonium ion is an intermediate in these processes.

Although the molecular rearrangements of tetra-aryl pinacols to pinacolones have been studied extensively with respect to the relative migratory aptitudes of the aryl groups,[3] the kinetic characteristics of these reactions have received comparatively little attention. The rearrangement of 4,4',4'',4'''-tetrachlorobenzopinacol and of the corresponding epoxide in acetyl chloride was studied kinetically by Meerburg[4] with the aid of an analytical method which involved measurement of the alcoholic alkali consumed by cleavage of the pinacolone. At 30° he observed fluctuations in the concentration, or apparent concentration, of the ketone for which he was unable to account. He concluded, however, that the epoxide could not be an intermediate in the rearrangement of the pinacol. The kinetics of the rearrangement of cis- and trans-1,2-diphenylacenaphthene-1,2-diol in acetic acid has been the subject of three investigations[5] in all of which the progress of reaction was followed by analysis for unchanged pinacol by oxidation with lead tetraacetate. The results of these investigations are not completely conclusive, particularly with respect to the ability of the trans isomer to undergo rearrangement.

In its gross aspects the mechanism of the pinacol rearrangement is firmly established.[6] However, there are numerous detailed features of these reactions which have been inadequately investigated, particularly in the tetraaryl pinacols in which the shift is to a tertiary carbon atom. These include the stereochemical changes at the migration terminus, the effect of substituent groups upon energy and entropy of activation, and the relative importance in the transition state of the carbonium ion (IV) and the phenonium ion[7] (V). The tetraaryl-ethylene oxides (II) have received only scant attention and there is inadequate experimental support for the commonly held opinion that the rearrangements of the epoxides and of the corresponding pinacols are completely analogous. Some of these problems are under investigation in this Laboratory. The present communication records the results of the kinetic study of the rearrangement of benzopinacol (I) and of tetraphenylethylene oxide (II) to β-benzopinacolone (III) in acetic acid with perchloric acid as the catalyst.
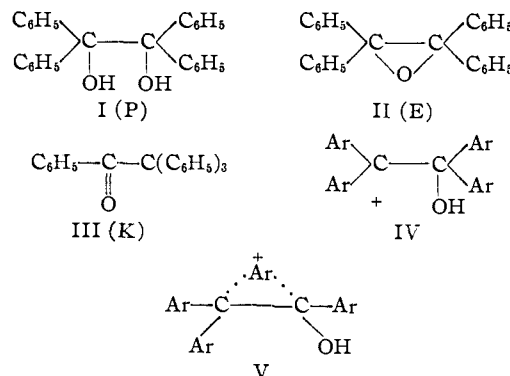
Experimental Part

Materials.—Glacial acetic acid (Mallinckrodt Chemical Works, bichromate test grade) was further purified by the method of Orton and Bradfield[8] modified by omission of acetic anhydride. The acid was distilled through an 18-

(1) Presented before the Division of Organic Chemistry, American Chemical Society, Atlantic City, N. J., September, 1952; Abstracts of Papers 24 M.

(2) Shell Oil Co., Wood River, Ill. This paper is abstracted from the Ph.D. Thesis of Herbert J. Gebhart, Jr., St. Louis University, June, 1952.

(3) For an excellent review of the pinacol rearrangement see G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 451–534.

(4) P. A. Meerburg, Rec. trav. chim., 24, 131 (1905); 28, 267, 270 (1909).

(5) P. D. Bartlett and R. F. Brown, This Journal, 62, 2927 (1940); R. Criegee and K. H. Plate, Ber., 72B, 178 (1939); H. Sello, University Microfilms, Ann Arbor, Mich., Pub. No. 1286 (1949).

(6) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapt. IX.

(7) D. J. Cram, This Journal, 71, 3863, 3875 (1949).

(8) K. J. P. Orton and A. E. Bradfield, J. Chem. Soc., 983 (1927).

inch Widmer column in which the spiral packing had been replaced by glass helices. The first 15% of the distillate was rejected. The main fraction was redistilled and the fraction of boiling range 117.0–118.1° was collected. The melting point of the product was consistently within the range of 16.20–16.40°. The water content was calculated on the basis of a freezing point depression of 0.2° per 0.1% by weight of water.[9] In the later stages of the investigation more nearly anhydrous acid was obtained by carrying out the second distillation as an azeotropic distillation with benzene.[10] The small residual water content was determined by titration with Karl Fischer reagent.[11] The purified acid was collected and stored in all-glass equipment and was protected from contact with atmospheric moisture.

Benzopinacol and benzopinacolone were prepared by the method of Bachmann.[12] The pinacol was recrystallized from a benzene–petroleum ether mixture until a 0.02 M solution in benzene was optically clear when examined at a wave length of 3300 Å. in a 1-cm. quartz cell in a Beckman model DU spectrophotometer. The product melted sharply at 195–196° on a pre-heated hot-stage. The pinacolone was recrystallized from benzene–petroleum ether until a constant molar extinction coefficient was obtained at 3300 Å.; m.p. 180–181°. Tetraphenylethylene was prepared from benzopinacolone by the method of Bachmann[13] and was converted to tetraphenylethylene oxide by the action of perbenzoic acid[14] in chloroform at room temperature for four days. The oxide was recrystallized from a 10–1 mixture of anhydrous ethanol and chloroform until a 0.02 M solution in benzene was optically clear at 3300 Å.; m.p. 205–206°.

The standard stock solution of perchloric acid was prepared by the dilution (1:100) of 70% aqueous perchloric acid with glacial acetic acid. This solution, approximately 0.12 M, was standardized by titration with a standard solution of sodium acetate in acetic acid with brom phenol blue.[15] The standard sodium acetate was prepared by dissolving primary standard grade of sodium carbonate in glacial acetic acid.

Analytical Methods.—Benzopinacol was estimated by oxidation with lead tetraacetate.[16] A 5.00-ml. sample of the solution to be analyzed was mixed in a 250-ml. glass-stoppered flask with an equal volume of an acetic acid solution which was approximately 0.06 N in lead tetraacetate and 1.0 N in potassium acetate. A blank was prepared in the same manner by replacing with acetic acid the solution of the pinacol. The solutions were allowed to stand at room temperature for two hours and were then analyzed for lead tetraacetate[17] by the addition of potassium iodide (0.5 g.), sodium acetate (6.0 g.) and 100 ml. of water. The liberated iodine was titrated with 0.04 N sodium thiosulfate.

Benzopinacolone was estimated by measuring the optical density in a 1.00-cm. quartz cell at a wave length of 3300 Å. of the solution obtained by the dilution of 5.00 ml. of the acetic acid solution of the ketone to 25.00 ml. or 50.00 ml. with t-butyl alcohol. The molar extinction coefficient of pinacolone was measured in the same solvent mixture. The mean value of 16 independent measurements of the molar extinction coefficient was 259 ± 2 l./mole-cm.

Reaction Rate Measurements.—An oil-bath, the temperature of which could be controlled to ±0.05°, was used. The reaction flask was of 250-ml. capacity and was equipped with two necks about 6 inches long. A pipet sealed to a three-way stopcock was fitted into the ground glass joint at the top of one of the necks to permit removal of samples

without opening the flask. The second neck was used for the introduction of the sample and catalyst, and was closed with a ground glass stopper vented to the atmosphere through a drying tube. Acetic acid was siphoned into the reaction flask and the quantity determined by weighing. The weighed sample of the pinacol or oxide was then dissolved in the acetic acid. The flask was immersed in the oil-bath almost to the top of the side arms. The pipet was inserted in one neck and a thin-bottomed tube containing the measured volume of the catalyst solution was suspended in the second neck. At least one hour was allowed for the flask and contents (including the catalyst solution) to reach bath temperature. The reaction was started by pushing a glass rod through the bottom of the catalyst tube. At appropriate times samples were removed by aspiration into the pipet and delivery into test-tubes containing a small drop of a concentrated solution of potassium acetate. The neutralization of the perchloric acid immediately stopped the reaction. The samples were cooled to 25.0 ± 2° and analyzed. Reaction rate constants usually were evaluated by the graphical method.

Isolation of Tetraphenylethylene Oxide Intermediate. Benzopinacol (2.50 g.) was dissolved into 225 ml. of 98.83% acetic acid, the solution was heated to 75° and the perchloric acid catalyst was added. The solution was 0.0296 M in pinacol and 0.0123 M in perchloric acid. After 15 minutes at 75° the reaction was stopped by the addition of potassium acetate and the solution was cooled to 25°. A 15-ml. portion was removed and analyzed for pinacol and pinacolone. The concentrations were found to be 0.0067 M and 0.0093 M, respectively. The remaining portion of the reaction mixture was seeded with a crystal of tetraphenylethylene oxide. Within 20 minutes needle-like crystals characteristic of the oxide began to separate. The mixture was allowed to stand at 25° for 15 hours. The precipitate was collected, and after washing with cold acetic acid and drying over potassium hydroxide weighed 0.34 g. The melting point (200–202°) was raised to 204–207° by admixture with an authentic sample of tetraphenylethylene oxide (m.p. 206–207°). Recrystallization of the crude product from acetic acid raised the melting point to 202–204°. The filtrate contained 0.64 g. of the oxide, calculated upon the basis of a solubility of 2.9 g. per liter. The latter was estimated by subjecting to rearrangement a saturated solution of the oxide and determining the concentration of pinacolone by the spectrophotometric method.

Interpretation of Kinetic Data

Evidence for Tetraphenylethylene Oxide Intermediate.—The data of Table I for a typical pinacol rate experiment show that the pinacol concentration $[P]$ decreases with time t in accordance with the first-order rate equation

$$-d[P]/dt = k_p[P] \qquad (1)$$

However, the rate of formation of pinacolone is slower than the rate of disappearance of pinacol, indicating appreciable storage of an intermediate (curve C of Fig. 1). If $[K]$ is the pinacolone concentration, the apparent pinacol concentration (which would equal the experimental value if there were no intermediate) is $[P]_0 - [K]$. Curve B of Fig. 1 shows that the instantaneous value of k_e defined by the equation

$$-\frac{d([P]_0 - [K])}{dt} = \frac{d[K]}{dt} = k_e([P]_0 - [K]) \qquad (2)$$

initially increases with time and terminally becomes constant as $[P] \to 0$. If the intermediate is tetraphenylethylene oxide and if no other kinetically detectable intermediate is present, then it follows that in a solution in which $[P] \approx 0$, $d[K]/dt = -d[E]/dt$ and

$$-d[E]/dt = k_2([E]_0 - [K]) \qquad (3)$$

in which $[E]$ is the concentration of the epoxide. The validity of equation 3 is supported by the data

(9) L. de Visser, Rec. trav. chim., 12, 101 (1893).

(10) D. S. Noyce and P. Castelfranco, THIS JOURNAL, 73, 4482 (1951).

(11) J. Mitchell, Jr. and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948.

(12) W. E. Bachmann in A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 71, 73.

(13) W. E. Bachmann, THIS JOURNAL, 56, 449 (1934).

(14) G. Braun in H. Gilman and A. H. Blatt, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 431.

(15) S. Winstein, E. Grunwald and L. L. Ingraham, THIS JOURNAL, 70, 821 (1939).

(16) R. Criegee, E. Büchner and W. Walther, Ber., 73, 571 (1940).

(17) N. H. Furman, "Scott's Standard Methods of Chemical Analysis," Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1939, p. 525.

TABLE I

REARRANGEMENT OF 0.01454 M BENZOPINACOL AT 75° IN ACETIC ACID CONTAINING 6.22 × 10⁻⁴ M PERCHLORIC ACID AND 1.0% OF WATER

Time, sec.	0.0395 N Na₂S₂O₃, ml.	Pinacol, M × 10³	k_p × 10⁴, sec.⁻¹	Optical density at 330 mμ	Pinacolone, M × 10³	Tetraphenyl-ethylene oxide, M × 10³	k_1 × 10⁴ sec.⁻¹, calcd.[a]
120	3.44	13.55		0.019	0.37	0.62	3.8
600	2.69	10.58	5.15	.046	0.89	3.07	4.4
1200	1.98	7.83	5.08	.093	1.79	4.92	4.3
1800	1.46	5.76	5.09	.148	2.85	5.93	4.3
2400	1.07	4.23	5.10	.207	3.98	6.33	4.3
3000	0.82	3.24	4.91	.262	5.05	6.25	4.1
3900	.52	2.06	4.98	.337	6.49	5.99	4.1
4800	.37	1.46	4.99	.405	7.80	5.28	4.0
6120	.21	0.83	(4.66)	.492	9.47	4.24	Av. 4.2
7200	.15	.59	(4.61)	.550	10.58	3.37	
9000	.10	.40	(4.99)	.614	11.82	2.32	
10,800			Av. 5.04 ± 0.14	.662	12.71		
13,860				.711	13.2		
16,800				.736	14.2		
19,200				.743	14.3		

[a] Calculated with the aid of equation 7 and the following values of the rate constants: k_p = 5.04 × 10⁻⁴ sec.⁻¹; k_2 = 2.24 × 10⁻⁴ sec.⁻¹. The latter was obtained by interpolation in Fig. 2 for a solution of which H_0 = + 0.89.
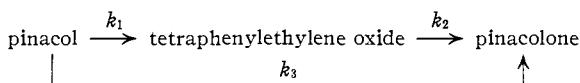
of Table II for a typical oxide rearrangement rate experiment. Tables III and IV summarize the effect of the catalyst concentration and of the water content of the solvent upon the rate constants k'_p, k'_e and k'_2.[18] Figure 2 shows the equality (for a particular solution) of k_2 and the terminal value of k_e, the rate constants in this graph being adjusted to 10⁻³ M perchloric acid. Confirmatory evidence concerning the identity of the intermediate was obtained by the isolation of tetraphenylethylene oxide in the expected quantity from a solution of the incompletely rearranged pinacol.

TABLE II

REARRANGEMENT OF TETRAPHENYLETHYLENE OXIDE AT 75° IN ACETIC ACID CONTAINING 2.83 × 10⁻⁴ M PERCHLORIC ACID AND 0.03% OF WATER

Time, sec.	Optical density, at 3300 Å. 1:5 dilution	Pinacolone, M × 10³	Oxide, calcd., M × 10³	k_2 × 10⁴, sec.⁻¹
0	0.000	0.000	6.005	
120	.037	0.714	5.29	1.06
360	.101	1.95	4.05	1.09
600	.147	2.84	3.17	1.06
840	.184	3.55	2.45	1.06
1080	.212	4.09	1.91	1.06
1320	.238	4.59	1.41	1.10
1560	.254	4.90	1.10	1.09
4200	.311	5.99	Av. 1.07 ± 0.02	

The Kinetics of First-order Consecutive Reactions with a Competing Simple Reaction.—The discussion which follows is based upon the assumption that pinacolone is formed by two kinetically distinguishable reaction paths, only one of which involves the oxide intermediate. The further assumptions are made that the three reactions are of

$$\text{pinacol} \xrightarrow{k_1} \text{tetraphenylethylene oxide} \xrightarrow{k_2} \text{pinacolone}$$
$$\underset{k_3}{\big|\text{_____}\big\uparrow}$$

(18) Throughout this paper primed rate constants are second order constants (or specific rates) calculated from the experimental first order constants by the relationship $k/[\text{HClO}_4]$ = k'.
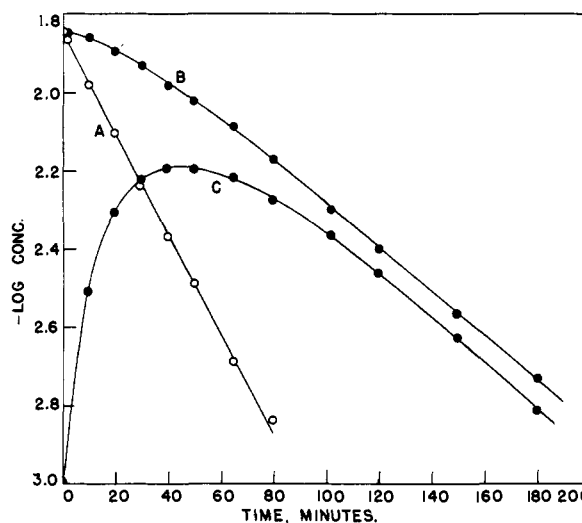

Fig. 1.—Graph of data of Table I showing variation with time of the concentration of benzopinacol (line A), of the apparent concentration of the pinacol as calculated from the pinacolone concentration ([P]₀ − [K]) (curve B), and of the concentration of the intermediate tetraphenylethylene oxide (curve C).

the first order with respect to the reactant and with respect to the perchloric acid catalyst and are irreversible. In view of the experimental demonstration that k_2 and k_p are first-order constants, it appears reasonable to assume that k_1 and k_3 also are first-order constants if k_p = k_1 + k_3. A reversible hydration of the oxide to pinacol is theoretically possible. This reaction is not kinetically detectable as shown by: (1) the absence of significant drifts with time of the instantaneous values of k_p and k_2; (2) our failure to detect any substance oxidizable by lead tetraacetate in reaction mixtures in which the oxide is undergoing rearrangement; and (3) the absence of any indication of a suppression of the oxide intermediate with increasing water content of the medium.

TABLE III

SUMMARY OF KINETIC DATA FOR THE PERCHLORIC ACID-CATALYZED REARRANGEMENT OF BENZOPINACOL IN AQUEOUS ACETIC ACID AT 75°

Water content,[a] % by wt.	Perchloric acid,[b] $M \times 10^4$	H_0[b] for $10^{-3} M$ HClO₄	Initial pinacol, $M \times 10^3$	$k_p \times 10^4$, sec.⁻¹	k'_p, l./mole-sec.	k'_e, l./mole-sec.	k'_1, calcd., l./mole-sec.
0.03 + 0.03	1.91	−0.51	18.0				
.03 + .04	2.85	− .46	22.7				
.10 + .02	3.89	− .31	10.6				
.13 + .02	0.701	− .24	11.5	3.08	4.65	1.87	4.0
.13 + .03	1.20	− .22	17.7	5.33	4.70	2.04	3.8
.13 + .03	1.80	− .22	17.0	7.90	4.65	1.88	4.0
.13 + .02	2.23	− .24	13.9	9.75	4.62	2.08	3.8
.20 + .03	4.10	− .07	18.8			1.32	
.31 + .04	5.02	+ .12	24.3	12.15	2.55	0.934	2.2
.48 + .03	1.89	+ .30	17.6	2.93	1.64	.661	1.3
.52 + .02	7.03	+ .33	8.82			.641	
.52 + .02	13.30	+ .33	9.81			.634	
1.00 + .02	6.22	+ .69	14.5	5.04	0.856	.366	0.70
1.91 + .02	55.2	+1.14	11.7			.137	
3.00 + .03	2.72	+1.57	18.8	0.348	0.134		

[a] The first figure in this column indicates the initial water content of the solvent and the second figure the water formed in the reaction. [b] The catalyst concentration and H_0 values are for 25°. The second-order constants k_p', k_e' and k_1' have been corrected for expansion of the solvent from 25° to reaction temperature with the aid of the volume–temperature data for acetic acid reported by D. Tyrer, *J. Chem. Soc.*, **105**, 2534 (1914).

TABLE IV

SUMMARY OF KINETIC DATA FOR THE PERCHLORIC ACID-CATALYZED REARRANGEMENT OF TETRAPHENYLETHYLENE OXIDE IN AQUEOUS ACETIC ACID AT 75°

Water content, % by wt.	Perchloric acid,[a] $M \times 10^4$	H_0 for $10^{-3} M$ HClO₄	Initial oxide, $M \times 10^3$	$k_2 \times 10^4$, sec.⁻¹	k_2', l./mole-sec.
0.03	2.83	−0.58	6.00	11.60	4.33
.03	1.88		6.13	7.55	4.25
.07	1.43	− .46	7.79	3.95	2.93
.08	3.19	− .42	6.69	8.01	2.68
.08	4.05		6.06	10.29	2.68
.15	4.14	− .23	5.95	7.14	1.82
.28	3.39	+ .01	4.79	3.88	1.21
.28	5.02		8.41	5.76	1.21
.52	8.20	+ .35	6.97	5.44	0.701
.92	11.7	+ .60	6.98	4.18	.378
1.00	22.9	+ .68	7.73	7.16	.331
1.03	21.7	+ .69	6.98	6.15	.299
1.87	55.6	+1.12	6.34	7.91	.150
1.89	55.1	+1.12	7.91	7.57	.145

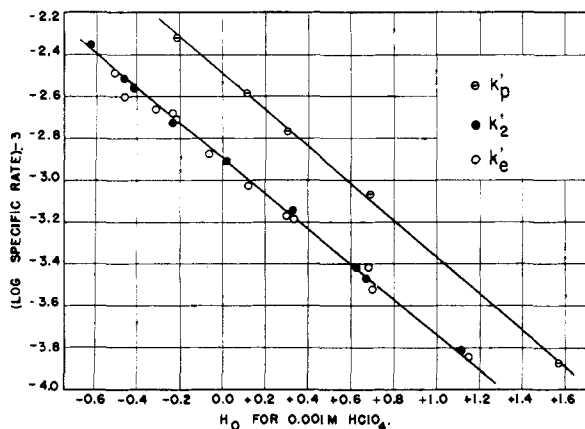[a] See footnote *b* of Table III.

Fig. 2.—Correlation of specific rates with the acidity function of the medium.

The mathematical treatment of irreversible first-order consecutive reactions[19] P → E → K is here modified to allow for the competing simple reaction P → K. The fundamental equations are

$$- d([P])/dt = k_1[P] + k_3[P] \quad (4)$$
$$d[E]/dt = k_1[P] - k_2[E] \quad (5)$$

Substitution into (5) of the value of [P] obtained by the integration of (4) yields

$$d[E]/dt + k_2[E] = k_1[P]_0 e \exp [-(k_1 + k_3)t] \quad (6)$$

The integration of (6) with the aid of the integrating factor $e \exp \int k_2 dt$ and evaluation of the constant of integration for the condition that [E] = 0 when $t = 0$ yields

$$[E] = [P]_0 \frac{k_1}{k_2 - k_1 - k_3} (e \exp[-(k_1 + k_3)t] - e \exp(-k_2t)) \quad (7)$$

On the assumption that $k_p = k_1 + k_3$ it is possible to evaluate k_1 and k_3 with the aid of (7) and the experimentally available values of k_p, k_2, $[P]_0$ and [E]. The results of these computations for a typical experiment are shown in Table I.

By differentiating (7) with respect to t and setting $d[E]/dt = 0$ an expression is obtained for t_{max} the time at which [E] is maximum

$$t_{max} = \ln [(k_1 + k_3)/k_2]/(k_1 + k_3 - k_2) \quad (8)$$

The data of Table I give a calculated value of t_{max} of 48 min., at which time [E] is $6.34 \times 10^{-3} M$. These agree satisfactorily with the experimental values shown in Fig. 1.

It should be emphasized that the observed rate of pinacolone formation cannot be accounted for in terms of the simplified reaction scheme in which the direct rearrangement of the pinacol is neglected. For example, when $t = 3900$ sec. (data of Table I) the assumption that $k_3 = 0$ and $k_1 = k_p$ leads to the calculated values ($M \times 10^3$): [P] = 2.04; [E] = 7.26; [K] = 5.28. With the values of the rate

(19) See, for example, S. Glasstone, "Textbook of Physical Chemistry," 2nd Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 1075.

constants given in Table I the corresponding values are [E] = 6.05 and [K] = 6.45. The latter are in satisfactory agreement with the experimental values.

Correlation of Rate Constants with Acidity Function.—For constant water content of the solvent the graph of k_p or k_2 vs. [A], the perchloric acid concentration, is linear and extrapolates to the origin, showing the absence of a solvent-catalyzed reaction. The following rate equations, in which the primed quantities are the second-order constants corresponding to the first-order constants of equations 1, 3 and 4, are valid at least over the range of values of [A] studied

$$- d[P]/dt = k_p'[A][P] = (k_1' + k_3')[A][P] \quad (9)$$
$$- d[E]/dt = k_2'[A][E] \quad (10)$$

With increasing water concentration and constant [A] the decreasing acidity of the medium leads to a corresponding decrease in the second-order constants. The plot of the Hammett acidity function H_0 values[20] shown in Tables III and IV against log $(10^{-3}k_2')$ is a straight line of slope -0.87. A similar correlation exists between H_0 and the experimental rate constant k_p' and the calculated constants k_1' and k_2'. The deviation of the slope from the theoretical value of unity may indicate that the fundamental assumption of acidity function measurements concerning the lack of dependence upon the base B of the activity coefficient ratio f_B/f_{BH^+} is not rigorously applicable to bases which differ in structure as much as do the nitroanilines (used for H_0 measurements) and benzopinacol. More probably the deviation is due to the use of H_0 values measured at 25° and rate constants measured at 75°.[21]
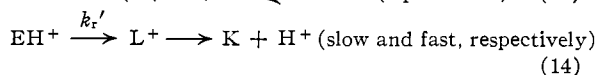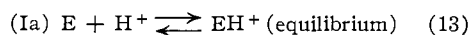
Because of the linear relationship between H_0 and log k' and the proportionality between k' and k equations 1 and 3 may be converted to the more general rate laws

$$-d[P]/dt = k_p''[P](h_0)^{0.9} = k_p''[P](\alpha_{H^+}f_B/f_{BH^+})^{0.9} \quad (11)$$
$$-d[E]/dt = k_2''[E](h_0)^{0.9} = k_2''[E](\alpha_{H^+}f_B/f_{BH^+})^{0.9} \quad (12)$$

in which h_0 is defined by the relationship $h_0 = -\log H_0$ and α_{H^+} represents the total activity of the protonated solvent molecules (H_3O^+) and H_2OAc^+) while the f terms are activity coefficients of the indicator base B and its conjugate acid BH^+.

Mechanism.—For the rearrangement of the epoxide E to pinacolone K the mechanism can be represented as

$$\text{(Ia)} \quad E + H^+ \rightleftharpoons EH^+ \text{ (equilibrium)} \quad (13)$$
$$EH^+ \xrightarrow{k_r'} L^+ \longrightarrow K + H^+ \text{ (slow and fast, respectively)} \quad (14)$$

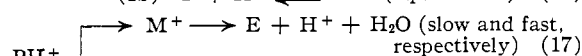where L^+ is the transition state complex. The Brönsted rate equation is

$$\text{rate} = k_r'[EH^+]f_{EH^+}/f_{L^+} = k_r[E]\alpha_{H^+}f_E/f_{EH^+} \quad (15)$$

(20) These H_0 values are from the measurements of F. J. Ludwig and K. H. Adams, This Journal, 76, 3853 (1954).

(21) A similar instance of a linear correlation of log k and H_0 in which the slope differs from unity by as much as 10% had been reported by E. A. Braude and E. S. Stern, J. Chem. Soc., 1976 (1948), and by F. A. Long, W. F. McDevit and F. B. Dunkle, J. Phys. Colloid Chem., 55, 829 (1951). On the other hand, using the same H_0 values as listed in Table III, F. J. Ludwig and K. H. Adams (unpublished work) have a perfect proportionality with log k for the perchloric acid-catalyzed dehydration of 1,1,2-triphenylethanol. These rate constants were measured at 40°.

in which k_r includes the rate constant k_r' and the equilibrium constant of (13). Since E and EH^+ differ in structure by a proton, as do B and BH^+, it is to be expected that the activity coefficient ratios f_E/f_{EH^+} and f_B/f_{BH^+} are at least approximately equal for a particular solvent. Hence, to the extent that this is true, equation 15 and the experimentally established rate equation 12 are equivalent.

Similarly, it can be shown that the experimental rate equations 9 and 11 are consistent with the following mechanisms for conversion of P to E and for the direct rearrangement of P to K
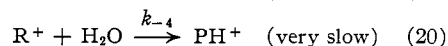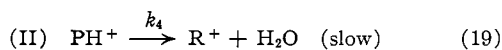
$$\text{(Ib)} \quad P + H^+ \rightleftharpoons PH^+ \text{ (equilibrium)} \quad (16)$$

$$PH^+ \begin{cases} \longrightarrow M^+ \longrightarrow E + H^+ + H_2O \text{ (slow and fast,} \\ \qquad\qquad\qquad\qquad\qquad\qquad \text{respectively)} \quad (17) \\ \longrightarrow N^+ \longrightarrow K + H^+ + H_2O \text{ (slow and fast,} \\ \qquad\qquad\qquad\qquad\qquad\qquad \text{respectively)} \quad (18) \end{cases}$$

The nature of the transition complexes L^+, M^+ and N^+ requires consideration. Since PH^+ undergoes two concurrent reactions the question arises whether M^+ and N^+ are the same or different. One possibility is that the transition complexes lead directly to the corresponding reaction products, the rate-determining dissociations of the C–O bond in PH^+ and EH^+ occurring simultaneously with the phenyl shift in the rearrangement and with ring closure in the epoxide formation. Complexes L^+, M^+ and N^+ would be represented by VI, VII and VIII, respectively, and the reactions might be

VI   VII   VIII
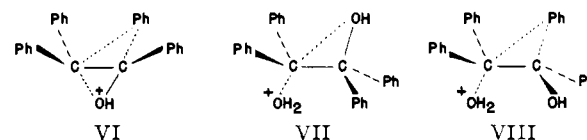
expected to show some evidence of neighboring group participation. If the reactions of PH^+ are thus composite in the activation step, as well as over-all, the values of the experimental activation energy E_a and of the free energy $\Delta F^{\ddagger}$ and entropy $\Delta S^{\ddagger}$ of activation calculated from k_p' (Table V) would have no significance[22] while the less precisely established corresponding values calculated from k_1' and k_3' would be of interest.

An alternate possibility is that the transition states lead to the unrearranged carbonium ion R^+ (VI) which is a common intermediate of sufficient stability to require additional small activation energies for the formation of EH^+ and KH^+. In this case M^+ and N^+ are essentially the same (except possibly for minor differences arising from the rotational configuration of the pinacol molecule as discussed below) and the activation thermodynamic quantities of interest are those computed from k_p' and k_2'. This alternate mechanism (II) may be represented by replacing equations 17 and 18 with the following

$$\text{(II)} \quad PH^+ \xrightarrow{k_4} R^+ + H_2O \text{ (slow)} \quad (19)$$
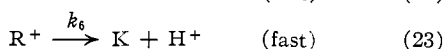$$R^+ + H_2O \xrightarrow{k_{-4}} PH^+ \text{ (very slow)} \quad (20)$$

(22) The problem of activation energy in composite reactions has been discussed by E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution," 2nd Edition, Oxford University Press, London, 1947, pp. 49-50 and 55-56.

TABLE V

THERMODYNAMICS OF ACTIVATION FOR REARRANGEMENT OF TETRAPHENYLETHYLENE OXIDE AND FOR THE REACTIONS OF
BENZOPINACOL IN ACETIC ACID CONTAINING 0.31% OF WATER

Rate constant	Temp., °C.	Specific rate,[a] l./mole-sec.	E_a, kcal./mole	$\Delta S^{\ddagger}$,[b] e.u.	$\Delta F^{\ddagger}$,[b] kcal./mole
k'_2	55	0.117 ± 0.002			
	75	$1.22 \pm .02$	26.0 ± 0.4	$+14.3 \pm 1.1$	20.37 ± 0.02
	85	$3.39 \pm .07$			
k'_p	55	$0.256 \pm .007$			
	75	$2.55 \pm .07$	26.0 ± 0.4	$+15.8 + 1.1$	$19.86 \pm .02$
	85	$7.27 \pm .20$			
k'_1	75	$2.07 \pm .06$	24.3 ± 1.1	9.5 ± 3.2	$20.0 \pm .1$
	85	$5.58 \pm .08$			
k'_3	75	$0.48 \pm .06$	31	26	$21.0 \pm .1$
	85	$1.72 \pm .08$			

[a] The rate constants in this table have been corrected for solvent expansion; see footnote b of Table III.   [b] Computed from the equation $k_{\text{rate}} = (kT/h)\, e \exp(-\Delta F^{\ddagger}/RT) = (ekT/h)\, e \exp(-E_a/RT)\, e \exp(\Delta S^{\ddagger}/R)$;   S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

$$EH^+ \xrightarrow{k_5} R^+ \qquad \text{(slow)} \qquad (21)$$

$$R^+ \xrightarrow{k_{-5}} EH^+ \qquad \text{(fast)} \qquad (22)$$

$$R^+ \xrightarrow{k_6} K + H^+ \qquad \text{(fast)} \qquad (23)$$

To bring this formulation into conformity with the kinetics it is necessary that $k_{-5} > k_6 >> k_{-4}$. The requirement that R^+ reacts predominantly by the internal processes of ring closure and rearrangement and is not sensitive to external attack by a solvent molecule seems not unreasonable for a molecule in which steric factors must be of major importance. The high susceptibility to acid-catalyzed hydration to the glycol which is characteristic of the phenyl-substituted ethylene oxides, including triphenylethylene oxide,[23] and the essentially complete failure of this reaction in tetraphenylethylene oxide suggests serious steric retardation in the latter reaction.

Mechanisms I and II represent limiting types. In view of the generalization that neighboring group participation tends to decrease with increasing phenyl substitution of the carbon atom at which heterolysis occurs[24] and in view of the opportunities for resonance stabilization of R^+ in the tetraaryl pinacols it may be expected that these substances react in a polar medium by a mechanism which approaches the limiting carbonium ion type. In the case of benzopinacol the stability of R^+ appears to be inadequate to allow it to be highly discriminating in its subsequent reactions, with the result that it reacts exclusively by one of the two internal processes available to it.[25] The predominance of ring

(23) J. L. Lane and D. R. Walters, THIS JOURNAL, 73, 4234 (1951).

(24) S. Winstein and E. Grunwald, ibid., 70, 828 (1948); S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, ibid., 74, 1113 (1952).

(25) With pinacols which can produce a more stable carbonium ion, external reactions with solvent molecules could compete more success-

closure relative to rearrangement probably reflects the rotational configuration of the pinacol molecule at the moment of reaction. If the pinacol assumes a favored rotational conformation it probably would be that having a *trans* arrangement of the hydroxyl groups since this would minimize the C–O dipole and phenyl–phenyl steric interactions. The molecule would be thus in a favorable state for epoxide formation. The minority of the molecules (*ca.* 20%) which undergo direct rearrangement would be those having the somewhat less stable *cis* configuration. The observed difference of approximately 1000 cal. in $\Delta F^{\ddagger}$ for epoxide formation and rearrangement is consistent with this interpretation if it may be assumed that the two reactions have energetically similar transition states.

Consistent with mechanism II are the large positive values of the entropy of activation, which are in marked contrast to the values usually found (-5 to $+2$ e.u.) for solvolytic reactions in acetic acid which are known to be subject to neighboring group effects.[26]

A firmer decision regarding the relative importance of the two preceding mechanisms could be made with the aid of information concerning the extent to which the rate-determining ionization of PH^+ is accelerated by participation by C_β–OH or by C_β–phenyl and that of EH^+ by C_β–phenyl participation. Because experimental work in progress is designed to provide this information discussion of that subject will be reserved for a subsequent communication.

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fully with these internal reactions. Thus, etherification dominates rearrangement in methanol and ethanol solutions of cis- and trans-1,2-dimethyl-1,2-acenaphthenediol (R. F. Brown, ibid., 74, 428 (1952)).

(26) See, for example, the data of reference 24.