Discussion

As shown in Fig. 2, there is no difference in the electrophoretic mobility of lactogenic hormone prepared from either sheep or beef pituitary in the whole *p*H range studied. Both have an isoelectric point at *p*H 5.73. This merely indicates that the ratio of basic to acid groupings is identical in these proteins; it does not indicate that they necessarily have the same structural configurations. Their amino acid content may be very different and preliminary determinations of the tyrosine content do in fact indicate that the hormone derived from sheep pituitaries has less of this amino acid than that from beef. The fact that they can be distinguished, one from the other, by solubility studies suggests that the arrangement and number of polar and non-polar groups may be different.

Should our electrophoretic studies have shown that the mobilities of beef and sheep lactogenic hormone are different, we might justifiably have concluded that species specificity exists here. The fact that their electrophoretic mobilities are the same does not, however, allow one to conclude that there is no species specificity, since it has been shown[9] that proteins derived from different species may show the same electrophoretic behavior. It seems not improbable that slight differences in beef and sheep lactogenic hormone may be detected serologically with the help of the extremely delicate quantitative precipitin test used by Heidelberger[10] to differentiate thyroglobulins.

Summary

An attempt has been made to differentiate the lactogenic hormone prepared from sheep and beef pituitaries by electrophoresis experiments. The results show that they are not distinguishable by their electrophoretic behavior. They both have an isoelectric point at *p*H 5.73.

[9] Landsteiner, Longsworth and Van der Scheer, *Science*, **88**, 83 (1938).

[10] Heidelberger and Kendall, *J. Exptl. Med.*, **62**, 697 (1935).

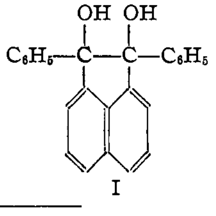
BERKELEY, CALIF. RECEIVED JUNE 27, 1940

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY AND THE BYERLY LABORATORY OF RADCLIFFE COLLEGE]

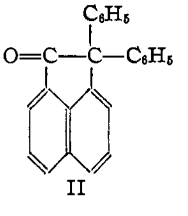
The Pinacol Rearrangement of *cis*- and *trans*-7,8-Diphenylacenaphthenediols-7,8

BY PAUL D. BARTLETT AND RONALD F. BROWN[1]

The fact[2] that both the *cis*- and *trans*-isomers of 7,8-diphenylacenaphthenediol-7,8 (I) undergo the pinacol rearrangement yielding the same product, 7,7-diphenylacenaphthenone (II), was the first apparent exception to the generalization[3,4] that in rearrangements of the pinacol type the migrating radical must displace the hydroxyl (or amino) group with Walden inversion.[5] This is a particularly interesting case, since this pinacol is free from the possibility of two reactions which, in the cyclic pinacols previously studied, compete with the migration of the substituents in the ring. Both ring contraction and simple dehydration are excluded by the nature of the five-membered ring of the acenaphthene system. We have therefore studied the rearrangements of these two isomers in some detail in order to gain information on the mechanism of the reaction. When our work was nearly completed, Criegee published some kinetic measurements on the same system which had been made several years previously.[6] We now report our work because the experiments performed were not entirely identical with those of Criegee and have led to theoretical conclusions of interest.



I



II

In common with Criegee, we followed the rearrangements of the isomers by titration with lead tetraacetate. Our runs were carried out in acetic acid containing various concentrations of water

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[1] Present address: Department of Chemistry, Purdue University, Lafayette, Indiana.

[2] (a) Beschke, Beitler and Strum, *Ann.*, **369**, 184 (1909); (b) Wittig, Leo and Weimer, *Ber.*, **64**, 2405 (1931); (c) Bachmann and Chu, THIS JOURNAL, **58**, 1118 (1936).

[3] Bartlett and Pöckel, *ibid.*, **59**, 820 (1937).

[4] Bernstein and Whitmore, *ibid.*, **61**, 1324 (1939).

[5] A part of the evidence for this generalization has been criticized recently by Meerwein, *Ann.*, **542**, 123 (1939). This case will be reviewed in a forthcoming paper from this Laboratory.

[6] Criegee and Plate, *Ber.*, **72**, 178 (1939).

and either *p*-toluenesulfonic or sulfuric acid or the solvent alone as catalyst, at 25°. Only those rearrangements in the presence of strong acid went fast enough for accurate measurement, and of these there were nine runs made on each isomer. The results with the two acids were entirely similar. In neither case was the rate of rearrangement strictly proportional to the acid concentration. The rearrangement of the *cis*-pinacol gave first-order kinetics under all conditions. When the results for the *trans*-pinacol in the solutions containing very little water were plotted as a unimolecular reaction, the plots approximated straight lines, but a slight curvature was evident. This curvature corresponded to acceleration as the reaction proceeded. Figure 1 shows the plots for the *cis*- and *trans*-pinacols with *p*-toluenesulfonic acid in the most anhydrous acetic acid used, where the *cis*-isomer reacts about six times as fast as the *trans*. In Fig. 2 the results of Criegee on a similar system at 30° are shown for comparison.

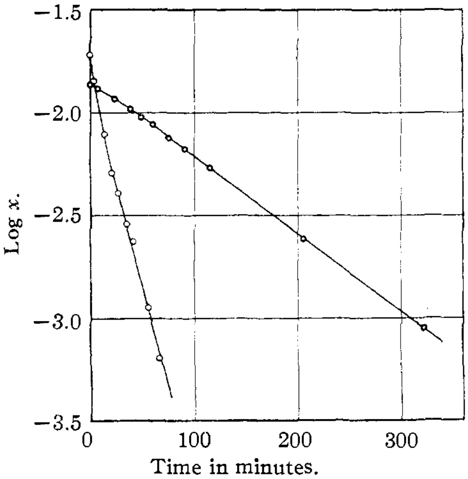


Fig. 1.—Run 10: O, *trans*; o, *cis*.

The effect of water in the solvent is threefold. It retards the rearrangement of both the *cis*- and *trans*-isomers, as shown in Table I. It makes the kinetics of rearrangement of the *trans*-pinacol deviate largely from the first order. Finally, it makes the *trans*-pinacol approach a limiting unimolecular rate identical with that of the *cis*-isomer. Figure 3 shows the unimolecular plots for the rearrangement of the isomers in the presence of 0.0275 *M* *p*-toluenesulfonic acid and 5.05 *M* water.

It is evident that the rearrangement of the *trans*-pinacol is not a simple, one-step process like that of the *cis*-pinacol. The identity of limiting rates in the presence of considerable water suggests a common intermediate in the rearrangement of the *cis*- and *trans*-pinacols. Such a situation would exist if the *trans*-pinacol were rearranging only by way of conversion into the *cis*-pinacol, and if this conversion were proceeding in the water-containing medium more rapidly than the rearrangement of the *cis*-isomer. If such were the case it should be possible to find *cis*-pinacol in a solution of partly rearranged *trans*-pinacol. We arrested the rearrangement of a 0.6060-g. sample of the *trans*-pinacol in acetic acid containing 5.41 *M* water, and 0.05 *M* sulfuric acid, at 28% completion (after eight hours). From the precipitated mixture the *cis*-pinacol

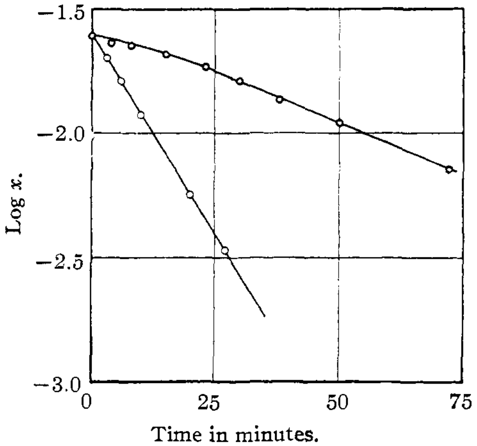


Fig. 2.—Criegee's runs no. 3 and 6: initial concentration of pinacols, 0.0250 *M*; *p*-toluene-sulfonic acid, 0.0250 *M*; water, 0.33 *M*; temperature, 30°: O, *trans*; o, *cis*.

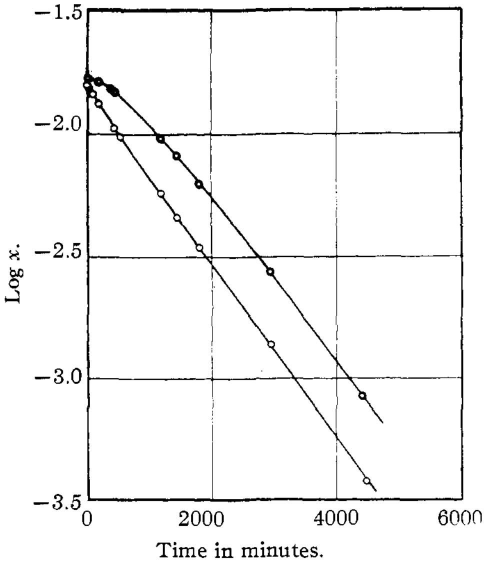


Fig. 3.—Run 12: O, *trans*; o, *cis*.

TABLE I[a]

UNIMOLECULAR VELOCITY CONSTANTS FOR THE PINACOL REARRANGEMENT OF *cis*- (C) AND *trans*- (T) 7,8-DIPHENYLACENAPHTHENEDIOLS-7,8 IN ACETIC ACID SOLUTION AT 25°

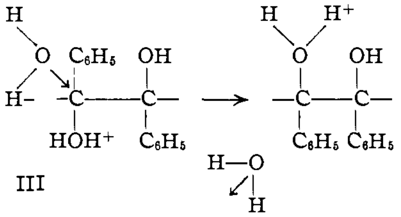
Run	Initial concn. of diol	Catalyst concn.	Water concn.	k_1
		No Catalyst		
1T	0.01844	0	0.25	0.00003
1C	.02001	0	.25	.00009
2T	.00648	0	.80	.00002
2C	.00743	0	.80	.0001
3T	.01929	0	2.88	.000002
3C	.00837	0	2.89	.000004
		Sulfuric Acid		
8T	0.01819	0.00439	0.17	0.0102
8C	.02248	.00438	.17	.0646
7T	.01369	.00875	.25	.0185
7C	.01888	.00872	.25	.0787
6T	.02241	.00477	.80	.0034
6C	.01478	.00479	.80	.0063
4T	.01964	.00955	.80	.0057
4C	.00730	.00959	.80	.013
5T	.02746	.00952	.79	.0058
5C	.01339	.00938	.80	.014
9T	.01729	.00423	2.81	.000460
9C	.01811	.00423	2.81	.00474
		p-Toluenesulfonic Acid		
10T	0.01371	0.0122	0.18	0.00866
10C	.01915	.0121	.18	.0465
11T	.02591	.0114	4.22	.000439
11C	.01731	.0115	4.24	.000492
12T	.01691	.0275	5.05	.000799
12C	.01574	.0275	5.05	.000824

[a] All concentrations are in moles per liter. The k_1 values for the runs on the *trans*-diol are the limiting values calculated for the last 20% of the reaction.

was isolated in a pure state in 20.6% yield in addition to the original *trans*-pinacol (7.6%) and the rearrangement product, 7,7-diphenylacenaphthenone (9.4%). It is thus established that in the course of rearrangement in acetic acid containing water, *trans*-7,8-diphenylacenaphthenediol-7,8 is converted into its *cis* isomer at a rate enough faster than the rearrangement to cause accumulation of the *cis*-pinacol. This means that it is unnecessary to assume, and indeed unlikely, that any rearrangement occurs without Walden inversion. A similar case has been reported by Suter and Milne.[7]

To follow this isomerization quantitatively and to account for the effect of water it would have been desirable to have a method of estimating the *cis*-pinacol in the presence of the *trans*-pinacol. Two such methods were tried without success. Advantage could not be taken of the faster reaction of the *cis* isomer with lead tetraacetate since both isomers react so rapidly that to differentiate between them requires impracticably dilute titrating solutions which render the iodine end-point indistinct. A melting point table of various mixtures of the isomeric pinacols and the pinacolone gave some promise of success, but the method was neither reproducible nor sensitive enough for the purpose. Even the integration of an exact kinetic equation for this case of successive catalyzed unimolecular reactions was not accomplished. We can, however, give a qualitative explanation of the effect of water on the kinetics of the reaction, based upon the demonstration that the *trans* pinacol is converted into the *cis*-pinacol.

The explanation is as follows. The *trans* pinacol is incapable of rearrangement into 7,7-diphenylacenaphthenone, but is converted into *cis* pinacol when its conjugate acid (III) collides with a water molecule giving inversion of configuration:



The *cis* pinacol is so constituted that it can give the pinacol rearrangement with Walden inversion. The rearrangement does not require water, but goes most rapidly under the conditions of strongest acidity. Therefore the rearrangement is retarded by water, whose effect is to lower the acidity of the medium. The configurative inversion, on the other hand, depends both upon the acidity of the medium and upon the supply of water molecules. While an increased concentration of water lowers the acidity and hence the concentration of III, it also increases the frequency of the kind of collisions depicted. Thus the isomerization gains in proportion to the rearrangement as the water content of the medium is increased. Exactly how much it gains we do not know, since in the runs with little water the rate-determining step with the *trans* compound is its conversion to the *cis* isomer, while with 5-molar water the rate-determining step is the rearrangement of the *cis* pinacol.

If water were essential to the *trans–cis* isom-

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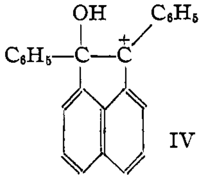
(7) Suter and Milne, Cincinnati meeting of the American Chemical Society, April 9, 1940.

erization, we might expect that the *trans* diol in anhydrous acetic acid would be incapable of this reaction. Actually, however, it seems probable that acetic acid can take the place of water in this reaction, though much less efficiently, so that even in the improbable event of the complete exclusion of water the isomerization would still occur at a rate characteristic of the solvent. Even sulfuric acid would not be wholly unable to perform this function. There are, of course, at least two other explanations to be considered. One is that the *trans–cis* isomerization of the pinacol occurs, not by a Walden inversion mechanism, but through a carbonium ion (IV) which would be common to the two isomeric diols. The relative promotion of the isomerization by water is against this, as is also the consideration that such a carbonium ion might be expected to rearrange directly to the pinacolone. The other possible interpretation of the facts is that the *trans–cis* isomerization is limited to solutions containing water, and that when the water content becomes low the *trans* pinacol begins to rearrange directly, without Walden inversion. This explanation is not excluded by the facts, but it seems less attractive than the one we have given because it involves the simultaneous operation of more different mechanisms than seem necessary to interpret the experiments.



IV

Experimental Part

Attempts to prepare *trans*-**7,8-diphenylacenaphthenediol-7,8** according to Wittig[2b] by the reaction of phenylmagnesium bromide with 1,8-naphthalic anhydride failed. It was prepared in 81% yield by the action of phenylmagnesium bromide on acenaphthenequinone following the directions of Bachmann and Chu.[2c] On recrystallization from alcohol a melting point of 158.7–159.0°, cor., was obtained. Acree[8] reported m. p. 154°; Bachmann,[2c] m. p. 154.3–155.3°; Beschke[2a] and Wittig,[2b] m. p. 155–156°; and Criegee,[9] m. p. 155.5–156.5°.

Anal.[10] Calcd. for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 84.88; H, 5.37.

1,8-Dibenzoylnaphthalene was prepared from the *trans* pinacol by the method of Bachmann.[2c]

cis - **7,8 - Diphenylacenaphthenediol - 7,8** was prepared from 1,8-dibenzoylnaphthalene according to Wittig[2b] with an average yield of the crude material of 70%. The pinacol was rather difficult to free from the last traces of diphenyl formed in the Grignard reduction as shown by the poor melting point of 171°. Several unsuccessful attempts were made to reduce the 1,8-dibenzoylnaphthalene by the magnesium–magnesium iodide system of Gomberg and Bachmann without success. However, on using high dilution and heating the reaction mixture for twelve to eighteen hours under reflux the *cis*-pinacol was obtained in 95% yield. Recrystallized from carbon tetrachloride, the material melted at 177.5–178.0°, cor. Wittig reported m. p. 171–173°, Bachmann, m. p. 173.5–175.6°, and Criegee, m. p. 176–177°.

Anal.[10] Calcd. for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 84.77; H, 5.23.

In taking the melting point of the *cis* pinacol, it was noted that although there was no decomposition on melting, yet within a minute the melt turned red. Five-tenths gram of the *cis* pinacol was placed in a test-tube and heated to 180° by means of an oil-bath for a period of one hour while under a pressure of 12 mm. When cooled and the vacuum released, the orange polymeric-like solid was dissolved in carbon tetrachloride from which a small amount of slightly yellow plates was obtained, m. p. 189.8–190.4°, cor.; mixed melting point with 1,8-dibenzoylnaphthalene, 189.6–190.1°, cor. The red mother liquor indicated the presence of 7,8-diphenylacenaphthylene. By using a Tswett column with calcium carbonate as the adsorbent, alcohol as the solvent, and acetone as the developer, a few milligrams of red needles was obtained, m. p. 155–158°, mixed melting point with a known sample of 7,8-diphenylacenaphthylene 157–160°. The effect of heat on the *trans* pinacol was not tried as above, but observations on its behavior when taking melting points indicated that it was much more stable to heat. This disproportionation and dehydration is similar to that noted first by Zincke[11] with benzopinacol.

It was of interest to establish the effect of alkali on the pinacols, since bases like heat cause the same type of cleavage with benzopinacol.[12] The *trans*-pinacol (0.5 g.) was heated under reflux in 10% alcoholic potassium hydroxide for one hour, and precipitated by pouring into water. There was no color change and the material was recovered unchanged on crystallization from alcohol. The *cis*-pinacol on similar treatment was unchanged also.

7,7-Diphenylacenaphthenone for reference purposes was obtained in quantitative yields by the action of a few drops of a strong acid such as sulfuric added to a boiling solution of either of the pinacols in glacial acetic acid. After five minutes the solution was poured into water, the precipitate collected, washed with water, and crystallized from alcohol, m. p. 175–176°, cor. The constitution of this pinacolone has been shown by synthesis.[2c]

The preparation of **7,8-diphenylacenaphthylene epoxide** was attempted by treatment of 7,8-diphenylacenaphthylene, prepared according to Bachmann, with perbenzoic acid in chloroform solution. The products isolated and identified by mixed melting point from the difficultly sepa-

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[8] Acree, *Am. Chem. J.*, **33**, 180 (1905).

[9] Criegee, Kraft and Rank, *Ann.*, **507**, 159 (1933).

[10] This analysis performed by Miss E. J. Cook.

[11] Zincke, *Ber.*, **10**, 1474 (1877).

[12] Bachmann, THIS JOURNAL, **55**, 391 (1933).

rable mixtures which resulted were *cis* pinacol, the pinacolone, 1,8-dibenzoylnaphthalene, and 7,8-diphenyl-7,8-dichloroacenaphthene. Wittig[13] also failed to obtain the epoxide by this method. An attempt to hydrolyze the dichloride with potassium hydroxide in 30% alcohol gave only 7,8-diphenylacenaphthylene, whereas it was hoped that the *trans* chlorohydrin and epoxide would be produced. Treatment of the magnesium salt of the *trans* pinacol, formed by the action of phenylmagnesium bromide on acenaphthenequinone, with the calculated amount of *p*-toluenesulfonyl chloride to obtain the monosulfonic acid ester also gave a mixture from which only the pinacolone could be isolated. Allowing the diphenylacenaphthylene to stand for several weeks in a glacial acetic acid solution of chromic anhydride gave only the 1,8-diketone.

All materials used in the rate studies of the rearrangement of the pinacols were obtained and purified by the usual methods. The water content of the glacial acetic acid used was determined by the freezing point method. The pure *p*-toluenesulfonic acid monohydrate was weighed out, dissolved in acetic acid of known water content, made to volume, and used without further standardization. Standardized sulfuric acid solutions both in acetic acid and in water were employed. Sodium thiosulfate and lead tetraacetate solutions were standardized against iodine as the primary standard. All volumetric apparatus was calibrated.

The *cis* and *trans* pinacols were weighed by difference into labeled 125-ml. Pyrex bottles with finely ground glass stoppers and 100.5 ml. of acetic acid of known water content added from a buret. The pinacols dissolved slowly on shaking. The bottles were placed in a thermostat held at 25.00 ± 0.01° for at least fifteen minutes, and the desired amount of water and catalyst added from a measuring pipet. The bottles were shaken vigorously for a moment and returned to the thermostat. The addition of the catalyst was taken as the starting time for the reaction. In calculating the volume of the resulting solution for determining the concentrations of the various components, the density of the pinacols was assumed to be 1.0, and the volume of the solution considered to be the sum of the volumes of all components. Except with water, the error so introduced was less than one part in a thousand. With water, the larger error due to the contraction in volume when acetic acid and water were mixed was corrected by calculation of the shrinkage in volume of the solutions from the density-weight per cent. table.[14]

The concentration of the pinacols during the rearrangement was followed by removing aliquots of 5.004 ml. with a pipet and adding to 0.5 ml. of a 10% solution of sodium acetate in acetic acid to stop the reaction. A 4.954-ml. portion of 0.05554 *N* lead tetraacetate solution was added and the flask allowed to stand at least a minute if the pinacol were the *cis* isomer, or for one hour, if the *trans* isomer.[6,9] At the end of the stated time, 5 ml. of a 40% solution of sodium acetate containing 2% potassium iodide was added. The iodine liberated by the excess lead tetraacetate was titrated with 0.02133 *N* sodium thiosulfate solution to the starch end-point and the concentration of the pinacol calculated. The large amount of sodium acetate used prevented the precipitation of lead iodide and lead sulfate, when sulfuric acid was the catalyst, both of which tend to make the end-point obscure.

The data for one run, No. 12T, are given in detail in Table II.

TABLE II[a]

RUN NO. 12T

All concentrations are given in moles per liter. 0.6516 g. of *trans* pinacol used. Concentration of *p*-toluenesulfonic acid, 0.0275 *M;* of water, 5.05 *M;* total volume of solution at start, 113.9 ml.

Time, min.	0.02133 *N* $Na_2S_2O_3$, ml.	Concn. of pinacol, *x*	Log *x*	% reaction
0	...	0.01691	8.2281	0
33	2.525	.01673	8.2235	1
79	2.555	.01660	8.2201	2
176	2.595	.01643	8.2156	3
375	2.875	.01524	8.1830	10
445	2.980	.01479	8.1700	12
1181	4.185	.00965	7.9845	42
1437	4.525	.00820	7.9138	51
1794	4.975	.00628	7.7980	63
2928	5.805	.00275	7.4393	84
4397	6.250	.00085	6.9294	95

[a] The first order reaction constant, k_1, calculated from the last three points is 0.000728 and 0.000799. This run is shown plotted for a first order reaction in Fig. 3.

A melting point curve for mixtures of the *trans* pinacol with the pinacolone was constructed. By mixing varying amounts of pure solutions of the two in acetic acid and precipitating by pouring into water, the material was obtained as an intimate mixture. Also it duplicated the method used in taking samples for melting point determination during a rearrangement. After collection, washing and drying, the melting points were determined with a Hershberg[15] apparatus. From the melting points of the various samples taken by reference to the melting point curve, the mole per cent. of the *trans* pinacol present was estimated and compared to the values as shown by titration. The results are shown in Table III.

TABLE III

MELTING POINT DETERMINATIONS

Run	Time, min.	M. p., °C.	Mole per cent.	Mole per cent. actual	Deviation
2	1432	155–159	100	98	2
2	5467	146–147	91–93	98	− 6
5	158	141–142	53–54	53	0
5	257	150–155	44–49	27	20
6	403	166	26	39	−13
8	85	157–158	40–42	45	− 4
8	121	160–161	36–37	31	5
				Sum	4

One run was made on the oxidation of a mixture of the *cis* and *trans* isomers by lead tetraacetate. The *trans* pinacol (0.0033 g.) and the *cis* pinacol (0.0002 g.) were weighed into a weighing bottle and dissolved in 10 ml. of glacial acetic acid. The solution was transferred to a 100-ml. volumetric flask, made up to approximately 95 ml. and placed in a thermostat held at 25° for fifteen

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(13) Wittig and Henkel, *Ann.*, **542**, 130 (1939).

(14) "I. C. T.," Vol. III, p. 123.

(15) Hershberg, *Ind. Eng. Chem.*, *Anal. Ed.*, **8**, 312 (1936).

minutes. One milliliter of 0.0236 N lead tetraacetate in acetic acid was added, the solution brought to volume, thoroughly mixed by shaking, and replaced in the thermostat.

The course of the reaction was followed in the usual manner by titrating the iodine, liberated by the lead tetraacetate remaining, with 0.00294 N sodium thiosulfate, from a 2-ml. micro-buret graduated in 0.01 ml. The starch end-point was so indistinct that the correct values could not be read off with the accuracy afforded by the apparatus. From the bimolecular plot it was impossible to determine whether a curvature existed or not.[16] The estimated straight line through the points gave a value for the bimolecular reaction constant of 540. Criegee[9] reported values of 284 at 20° and 682 at 30°.

A rearrangement of the *trans* pinacol was interrupted at an intermediate point and the substances present isolated. The *trans* isomer (0.6090 g.) was dissolved in 80 ml. of acetic acid in a 100-ml. volumetric flask, and placed in a thermostat at 25°. Ten milliliters of 1 N sulfuric acid in aqueous solution was added, the whole brought to volume with acetic acid, thoroughly mixed by shaking, and returned to the thermostat. After eight hours, the concentration of the pinacol, determined in the ordinary manner by titration, indicated that 28% reaction had occurred. The solution was poured into a large volume of water, allowed to stand for one hour to ensure complete coagulation of the precipitate, and filtered. The solid material collected was dissolved in alcohol to which a few drops of 10% sodium hydroxide solution had been added and separated by crystallization into four fractions. Each fraction was recrystallized from carbon tetrachloride and hexane. From the first fraction was obtained 0.054 g. of pure 7,7-diphenylacenaphthenone, m. p. 175–176°, mixed m. p. 175–176°. From the second and third fractions was obtained a total of 0.125 g. of pure *cis*-7,8-diphenylacenaphthenediol-7,8, m. p. 177.5–178.0°, mixed m. p. 177.5–178.0°. From the last fraction, 0.046 g. of the pure *trans* isomer was isolated, m. p. 158–159°, mixed m. p. 158–159°. Each of these products showed a large depression of the melting point when mixed with either of the others. The residues accounted for the remainder of the material. The conditions of the rearrangement, sulfuric acid, 0.05 M, water, 5.41 M, *trans* pinacol at the start, 0.0180 M, were purposely made similar to those of run 12, with the exception that sulfuric acid was used instead of *p*-toluenesulfonic acid.

We thank Dr. Saul Winstein for discussions which were helpful in the interpretation of these results.

Summary

With sulfuric or *p*-toluenesulfonic acid as catalyst and in acetic acid solution containing a minimal amount of water, *cis*-7,8-diphenylacenaphthenediol-7,8 (I) is rearranged into 7,7-diphenylacenaphthenone (II) about six times as fast as its *trans* isomer.

The rearrangement of the *cis* pinacol shows first-order kinetics under all conditions. If the concentration of water in acetic acid is increased, the rearrangement of the *trans* pinacol shows a steadily increasing deviation from first-order kinetics, and its final rate approaches that of the *cis* pinacol. Both rates are retarded by water.

This behavior suggests that the *trans* pinacol is isomerized into the *cis* pinacol prior to rearrangement, and this has been confirmed by the isolation of *cis*-7,8-diphenylacenaphthenediol-7,8 from a rearrangement of the *trans* isomer which had proceeded to the extent of 28%.

An explanation is given of the effect of water on the rate and order of the reaction. It is concluded that the *trans* pinacol, which is incapable of pinacol rearrangement with Walden inversion, cannot give this rearrangement, but can be isomerized by acid and water into the *cis* pinacol. This pinacol then rearranges rapidly in the absence of much water, but accumulates in the solutions having high water concentrations. Thus the rate-determining step at low water concentrations is the conversion of the *trans* pinacol into the *cis* isomer, while at high water concentrations it is the rearrangement of the accumulating *cis* pinacol.

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[16] Backer, *Rec. trav. chim.*, **57**, 967 (1938); van der Corput and Backer, *Proc. Acad. Sci. Amsterdam*, **41**, 1058 (1938).