

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

Studies on the Pinacol Rearrangement. IV. Competition Between Dehydration and Pinacol Rearrangement in the Reactions of the Isomeric 3,4-Bis-(*p*-acetoxyphenyl)-3,4-hexanediols with Acidic Reagents^{1a}

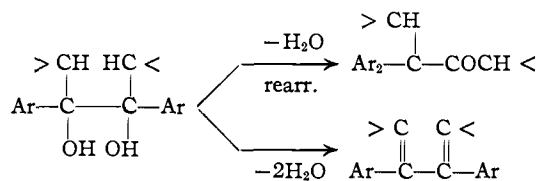
BY JOHN F. LANE AND LEONARD SPIALTER^{1b}

Studies on the pinacol rearrangement, and interfering side reactions, continue in this paper with an investigation of the behavior of *meso*- and *rac*-3,4-bis-(*p*-acetoxyphenyl)-3,4-hexanediols toward various acidic reagents: notably, (a) acetic anhydride, (b) formic acid, (c) sulfuric acid in acetic anhydride, (d) hydrogen chloride in acetic acid, (e) hydrogen chloride in acetic anhydride, and (f) mixtures of acetyl chloride and acetic anhydride. Of these, only reagents (e) and (f) effect dehydration to the dienestrol diacetates and derived substances. Reagent (a) is without effect, while reagents (b), (c) and (d) produce exclusively the pinacolone 4,4-bis-(*p*-acetoxyphenyl)-3-hexanone. The dehydration reaction appears to occur more easily with the *meso* than with the *racemic* form of the pinacol and is benefited by (i) low concentration of the pinacol in the dehydrating solvent, (ii) a high ratio of acetyl chloride to acetic anhydride and (iii) increase in temperature.

These results are discussed in terms of the modern theory of molecular rearrangements, and a mechanism is suggested for the dehydration reaction which involves preliminary formation of a monoacetate of the reacting pinacol.

The first two papers² of this series dealt with competition between pinacol rearrangement and certain side-reactions (formation of oxide and glycol) for the compound $\text{Ph}_2\overset{(a)}{\text{C}}\text{OH}\overset{(b)}{\text{C}}\text{HBrPh}$. Evidence was submitted to show that the extent of such side-reactions depended markedly on the capacity of the oxygen function at $\text{C}_\beta(\text{OH}, \text{O}^-)$ to compete with phenyl as a neighboring group which assisted departure of the bromide ion at C_α .

The present paper concerns itself with competition between the pinacol rearrangement and a different kind of side-reaction, namely, complete dehydration to a conjugated diene, in a system of the type



In this study, with the aid of analytical methods developed in Part III³ of this series, the composition of products arising from the action of a variety of acidic reagents on the *meso*- and *rac*-forms of 3,4-bis-(*p*-acetoxyphenyl)-3,4-hexanediol (II)⁴ has been determined. Of these reagents, which include (a) acetic anhydride, (b) formic acid, (c) sulfuric acid in acetic anhydride, (d) hydrogen chloride in acetic acid, (e) hydrogen chloride in acetic anhydride and (f) mixtures of acetyl chloride and acetic anhydride, only the last two cause detectable dehydration of either form of II to unsaturated substances. Acetic anhydride, even at its boiling point, has no appreciable effect upon the *meso* form of II. Reagents (b), (c) and (d) abstract water from both forms of II to give exclusively the product of pinacol rearrangement, 4,4-bis-(*p*-acetoxyphenyl)-3-hexanone (IV).

The interaction of both forms of II with hy-

drogen chloride in acetic anhydride has been studied at two temperatures, 50° and 100°. At both temperatures the *meso* isomer gives substantially less of the rearranged product, while the extent of rearrangement for both isomers decreases with the temperature. Thus, the product compositions in mole percentages of *U* (total monomeric unsaturates), *R* (rearranged product, IV) and *P* (polymerized dienes) were: (a) at 50°, *meso*: *U*, 59.5; *R*, 19; *P*, 21.5; *rac*: *U*, 62, *R*, 26; *P*, 12; (b) at 100°, *meso*: *U*, 93; *R*, 6; *P*, 1; *rac*: *U*, 80, *R*, 15; *P*, 5. The unsaturated fractions at 50° consumed the theoretical quantity of bromine; hence, could not have contained³ the acetates of β -dienestrol or indenestrol.

The reaction of the isomers of II with mixtures of acetyl chloride and acetic anhydride has been studied^{1a} as a function of three variables: (i) the composition of the dehydrating mixture, (ii) the ratio of dehydrating agent to pinacol and (iii) the temperature.

For the *racemic* isomer the amount of rearrangement decreased markedly with increasing acetyl chloride content of the medium. Thus, at 50° (89.5 hr.), with various volume ratios (γ) of acetic anhydride to acetyl chloride, the following results were obtained: (a) $\gamma = 5$: *U*, 60.4 \pm 1.1; *R*, 24.2 \pm 0.8; *P*, 15.4 \pm 1.2; (b) $\gamma = 1$: *U*, 77.8 \pm 2.8; *R*, 16.4 \pm 1.1; *P*, 5.8 \pm 1.7; (c) $\gamma = 0$: *U*, 94.6; *R*, 5.4; *P*, 0.

For this isomer, also, the amount of rearrangement decreased with increasing ratio of solvent to pinacol. Thus, at 50° (6 hr., $\gamma = 0.5$), the pinacol (100 mg.), gave with various volumes of solvent, the following percentages of products: (a) 0.40 ml.; *U*, 65.2 \pm 0.2; *R*, 27.4 \pm 0.7; *P*, 7.4 \pm 0.9; (b) 1.00 ml.: *U*, 65.3 \pm 2.3; *R*, 23.6 \pm 0.3; *P*, 11.1 \pm 1.6; (c) 2.00 ml.: *U*, 65.6 \pm 2.0; *R*, 19.8 \pm 1.0; *P*, 14.6 \pm 1.3.

For both isomers (II) increase in temperature benefited the dehydration reaction over the rearrangement, although the effect was more pronounced with the *racemic* than with the *meso* form. Thus at 30° (120 hr.) in pure acetyl chloride (1.00 ml./100 mg. of II) rearrangement occurred to the extent of 6.7% with the *meso* form and to the extent of 11.8% with the *racemic* form, while at 70° (24 hr.) the corresponding quantities were 3.7 and 4.2%, respectively.

(1) (a) For detailed tables supplementary to this article order Document 3259 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting \$1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or \$1.00 for photocopies (6 \times 8 inches) readable without optical aid. (b) du Pont Fellow in Rutgers University, 1948-1949.

(2) J. F. Lane and D. R. Walters, *THIS JOURNAL*, **73**, 4234, 4238 (1951).

(3) J. F. Lane and L. Spialter, *ibid.*, **73**, 4408 (1951).

(4) The same numbering system for compounds is employed in this paper as in Part III.

Experimental

Materials.—*meso*-II, m.p. 215–216°, and *rac*-II methanolate, m.p. 91–92°, prepared as previously described,³ were supplied by the White Laboratories, Inc., Newark, New Jersey. Acetyl chloride, b.p. 51.0–51.4° (755 mm.), was prepared by distillation of the C.P. product of the J. T. Baker Co. from dimethylaniline as recommended by Fieser.⁵ Acetic anhydride, b.p. 140–141° (770 mm.), was prepared by fractional distillation of the C.P. product of the Eimer and Amend Co.; formic acid, 98–100%, was the White Label Product of the Eastman Kodak Co.

Determination of Products.—Suitably purified (see below) mixtures of products from the action of dehydrating agents on the isomeric pinacols (II) were dissolved in benzene and subjected to chromatographic analysis as previously described.³ (In the succeeding text the four characteristic fractions will be designated as follows: (1) monomeric unsaturates, (2) pinacolone (IV), (3) pinacol (II) and (4) polymer.) The fractions (2), initially obtained as glasses, crystallized on treatment with petroleum ether to give materials melting in the range 88–90°, which were indifferent to the action of bromine in acetic acid containing potassium acetate, and which gave no depression of the melting point when mixed with authentic specimens³ of the pinacolone (IV). Bromometric analysis of the unsaturated fractions (1) for content in α - and γ -dienestrol was performed, as previously described.³ The fractions (4) were amorphous solids which absorbed bromine in the same fashion as did the α - and γ -dienestrol diacetates.

Action of Acetic Anhydride on *meso*-II.—*meso*-II, 654 mg., was covered with acetic anhydride, 5 ml., and the mixture was boiled under reflux for 90 minutes. A clear, colorless solution resulted, which on cooling deposited heavy crystals. These, after having been removed by filtration, washed with ether and dried, weighed 444 mg., m.p. 215–216°. The combined filtrate and ethereal washings were neutralized with aqueous sodium bicarbonate and extracted with ether. Evaporation of the ethereal extracts gave an additional 189 mg. of crystals, m.p. 210–214°: total recovery, 633 mg. (97%).

Action of Formic Acid on the Pinacols.—In each of two reaction tubes⁶ was placed 1.00 ml. of formic acid. To one tube was then added 100 mg. (0.256 mmole) of *meso*-II and to the other 100 mg. (0.239 mmole) of *rac*-II methanolate. The tubes were sealed and heated at 50° for four days. After removal of the solvent *in vacuo* the products were analyzed: *meso*, (1) 0; (2) 66.1 mg.; (3) 19.5 mg.; (4) 0; *rac*, (1) 0; (2) 60.7 mg.; (3) 19.8 mg.; (4) 0.

Action of Sulfuric Acid in Acetic Anhydride on the Pinacols.—To samples (100 mg.) of *meso*-II and *rac*-II methanolate were added separately 1.00-ml. portions of 1.5 *N* sulfuric acid in acetic anhydride. Immediate solution occurred in each case. After 10 minutes 180 mg. of anhydrous potassium acetate was added to each tube, and the contents of both were extracted independently with hot benzene. Chromatographic analysis gave: *meso*, (1) 0; (2) 82.0 mg.; (3) 8.0 mg.; (4) 0; *rac*, (1) 0; (2) 77.9 mg.; (3) 8.5 mg.; (4) 0.

Action of Hydrogen Chloride in Acetic Acid on the Pinacols.—Sealed tubes containing, respectively, 100 mg. of *meso*-II and of *rac*-II methanolate and 1.00 ml. each of 1.05 *N* hydrogen chloride in acetic acid were heated 1.5 hours at 50°. After evaporation of the solvent *in vacuo* the products were analyzed: *meso*, (1) 0; (2) 51.6 mg.; (3) 37.9 mg. (4) 0; *rac*, (1) 0; (2) 51.6 mg.; (3) 32.7 mg.; (4) 0.

Action of Hydrogen Chloride in Acetic Anhydride on the Pinacols.—Sealed tubes each containing 1.00 ml. of 1.18 *N* hydrogen chloride in acetic anhydride and, respectively, 100 mg. of *meso*-II and of *rac*-II methanolate were heated at 50° for 48 hours. After removal of the solvent *in vacuo* the analysis gave: *meso*, (1) 17.5 mg. (0.050 mmole, m.p. 103–116°, consumed 0.365 ml. of 0.146 *M* bromine); (2) 5.7 mg. (0.016 mmole); (3) 63.7 mg. (m.p. 215–216°); (4) 6.3 mg.; *rac*, (1) 48.3 mg. (0.138 mmole, consumed 0.955 ml. of 0.146 *M* bromine); (2) 20.1 mg. (0.055 mmole); (3) 8.9 mg.; (4) 9.6 mg. Repetition of the foregoing experiment, but with heating at 100° for 2.5 hours, gave: *meso*, (1) 82.0 mg.

(3) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1941, p. 380.

(6) These reaction tubes were soft glass test-tubes, 15 cm. \times 1 cm.

(7) Determined by Volhard analysis.

(0.234 mmole); (2) 5.7 mg. (0.016 mmole); (3) 1.1 mg.; (4) 0.9 mg.; *rac*, (1) 71.5 mg. (0.204 mmole); 13.8 mg. (0.038 mmole); 3.1 mg.; (4) 4.5 mg.

Action of Mixtures of Acetyl Chloride and Acetic Anhydride on the Pinacols.—In these experiments samples of 100 mg. of either *meso* or *rac*-II were placed in reaction tubes and the desired quantity (usually 1.00 ml.) of a mixture of acetyl chloride and acetic anhydride added. The tubes were then sealed and heated for various lengths of time in a thermostated bath. After removal of the solvent *in vacuo* the residues were taken up in benzene and subjected to chromatographic analysis. The results are given in Tables I, II and III.^{1a}

Yields of Titratable Diene at 70°.—In one experiment 5 samples of 100 mg. each of *meso*-II and *rac*-II were heated in sealed tubes for 48 hours at 70° with 1.00 ml. of a mixture of two parts of acetic anhydride to one of acetyl chloride. The same experiment was repeated, using as the dehydrating agent one part of acetic anhydride to two parts of acetyl chloride. After evaporation of the solvent *in vacuo*, each of the twenty samples was taken up in benzene and subjected to chromatography on silicic acid to remove the monomeric unsaturates (fraction 1). The five fractions (1) for each of the four sets of conditions were then combined and subjected to bromometric analysis³ for titratable diene. The results follow:

Pinacol, mmole	Vol. ratio, Ac ₂ O/AcCl	Diene, mmole	Ml. of 0.137 Br ₂ consumed	α, γ -Diene yield, %
<i>meso</i> , 1.33	2:1	1.24	8.61	84
	1:2	1.20	4.49	46
<i>rac</i> , 1.19	2:1	1.07	6.28	72
	1:2	1.12	2.19	25

Behavior of 4,4'-Bis-(*p*-acetoxyphenyl)-3-hexanone (IV) toward Acetyl Chloride and Acetic Anhydride.—Three sealed tubes, each containing 50.0 mg. of the pinacolone IV and, respectively, (a) 1.00 ml. of acetic anhydride, (b) 1.00 ml. of 1:1 acetic anhydride-acetyl chloride, and (c) 1.00 ml. of acetyl chloride, were heated at 110° for 60 hours. The tubes were cooled, opened, and the solvent slowly evaporated away during several days in a vacuum desiccator over potassium hydroxide. They were then pumped out with an oil-pump for a period of 40 hours until the weights of the residues reached a constant value. These glassy residues were then dissolved individually in 2.50 ml. of purified carbon tetrachloride and their infrared spectra³ compared with one obtained from 50 mg. of pure pinacolone IV in the same quantity of solvent. The four curves were all identical with each other and superimposable with congruence in both the position and height of every absorption maximum. The lack of additional bands in the first three cases, furthermore, indicated the absence of significant residues left from the medium itself.

Discussion

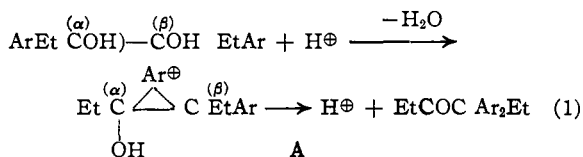
The most immediately apparent conclusion to be drawn from the foregoing experimental results is that the pinacol (II) undergoes dehydration to the diene only in systems containing acetyl chloride, *i.e.*, when the solvent is either a previously prepared mixture of acetyl chloride with acetic anhydride or acetic anhydride containing hydrogen chloride.⁹ Other solvents capable of proton donation to the pinacol cause its rearrangement to the pinacolone (IV), a process which, in terms of the modern theory of molecular rearrangements,^{2,10a,b,11} can be pictured as proceeding through the stages

(8) Determined, through the courtesy of the Department of Chemistry, Harvard University, on their Baird Associates infrared spectrograph.

(9) The "onium" salt Ac₂OH⁺Cl⁻, to be expected from the interaction of hydrogen chloride with acetic anhydride, has been shown by M. Usanovitch and L. N. Vasil'eva (*J. Gen. Chem., U. S. S. R.*, **16**, 1202 (1946); *C. A.*, **41**, 2976 (1947)) to exist in mobile equilibrium with acetyl chloride and acetic acid.

(10) (a) J. F. Lane and E. S. Wallis, *THIS JOURNAL*, **63**, 1674 (1941). (b) P. I. Pollak and D. Y. Curtin, *ibid.*, **72**, 961 (1950).

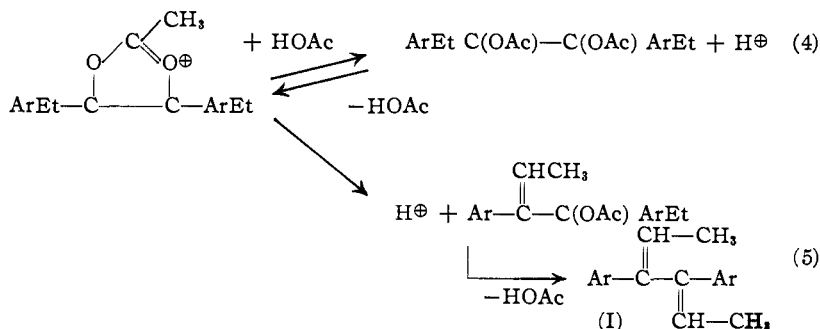
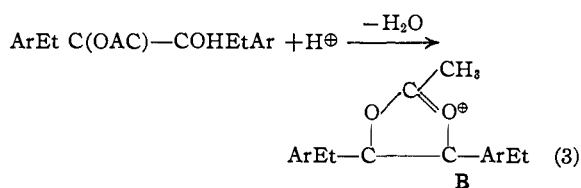
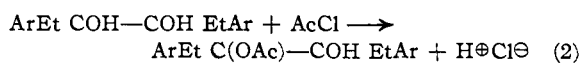
(11) D. J. Cram, *ibid.*, **71**, 3863 (1949).



It is also to be noted in this connection that, in mixtures of acetyl chloride and acetic anhydride, dehydration competes more favorably with rearrangement as the proportion of acetyl chloride increases. Indeed, in pure acetyl chloride it becomes nearly quantitative.

A possible interpretation of this interesting behavior is suggested by consideration of earlier studies² in this series which showed that certain side reactions accompanying the pinacol rearrangement can be correlated with the effectiveness of oxygen functions at C_β in competing with C_β-Ar as "neighboring groups"¹² which assist departure of a base from C_α. It is evident that in this system the grouping C_β-OH can play no significant role in such interference with the rearrangement, for the general action of acidic reagents is to produce exclusively the process (1) above. Should this grouping, however, first be transformed to C_β-OAc, then much more powerful interference would be expected, since the acetyl group may be expected to exert a driving force in such participation 3-4 kcal. in excess of that of C_β-OH or C_β-OCH₃.^{12,13} But this transformation is just that which is most likely to occur in the presence of a powerful acylating agent such as acetyl chloride.

Accordingly, a plausible mechanism is for the dehydration reaction, in our opinion



where the intermediate **B** possesses sufficient stability to compete favorably with **A** (which leads to rearrangement) and ultimately decomposes to give the highly conjugated, thermodynamically stable diene (I).

This interpretation, though admittedly tenta-

(12) Cf. S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948), for the general theory of the "neighboring group effect."

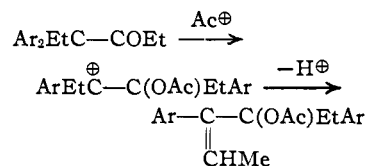
(13) S. Winstein, E. Grunwald and L. I. Ingraham, *ibid.*, **70**, 821 (1948).

tive, is in harmony with a number of observed experimental facts. First, the extent of dehydration increases with the availability of acetyl chloride which would be expected to facilitate process (2). Second, in more dilute solution the rearrangement of *rac*-II (added to the system as the methanolate) is suppressed (Table III). Now process (2), in the presence of excess acetyl chloride, should be pseudo-first-order (in the pinacol). The competing process (1), however, for which the protons are furnished by the reaction of methanol with the solvent, should be bimolecular (first-order in pinacol and in acid) and therefore should suffer much more markedly from dilution than (2). Finally, inspection of Tables II and IV shows that *meso*-II seems to be generally less susceptible to rearrangement than is *rac*-II methanolate under comparable conditions. On the basis of the above interpretation this is expected, since the intermediate **B**, formed (with Walden inversion) from the *meso*-isomer, has its two aryl groups in *trans*-juxtaposition, a configuration which should be less sterically strained than the *cis*-configuration resulting from the *rac*-isomer.^{10b}

In contrast to acetyl chloride, acetic anhydride seems to have no effect on the pinacol. So far as the results go they indicate that this substance functions chiefly as an inert solvent, any transformations which occur in it being attributable to the presence of proton donors¹⁴ (reaction 1) or of acetyl chloride (process 2).

The results on the yields of titratable diene at 70° deserve brief comment. They show that prolonged treatment of reaction mixtures rich in diene with solvents high in acetyl chloride content decreases markedly the amount of diene (presumably α and γ-dienestrol diacetates) which can absorb bromine. This, in our opinion, is probably to be attributed to increased formation of indenestrol "A" diacetate (III) under these conditions.

Finally we have considered the existence of a reverse rearrangement of the pinacolone IV to an intermediate capable of going over into the diene (I), as in a reaction of the type



This possibility has been ruled out, by examination of the infrared spectra of products resulting from treatment of the pinacolone IV with acetyl chloride and acetic anhydride in

sealed tubes for 60 hours at 110°. Quantitative comparison of these spectra with one obtained from pure IV demonstrated that no significant amount of reaction, either of interconversion or of some

(14) F. V. Wessely, E. Kerschbaum, A. Kleedorfer, F. Prillinger and E. Zajic, *Monatsh.*, **73**, 127 (1940), report that (non-acetylated) II is converted to IV by the action of potassium bisulfate and potassium pyrosulfate in acetic anhydride. This medium is apparently comparable in its action to the acetic anhydride-sulfuric acid of the present study.

other kind, such as acetylation of any enol of IV, occurred under even these fairly strong conditions.

Any interconversion of diene (I) to ketone IV is highly unlikely since the elements of water would have to be picked up from a strongly dehydrating medium.

Acknowledgment.—The authors wish to express their sincere thanks to E. I. du Pont de Nemours and Company, Wilmington, Delaware, for generous financial assistance in the academic year 1948–1949 which made this study possible.

NEW BRUNSWICK, NEW JERSEY

RECEIVED FEBRUARY 28, 1951

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF LOUISVILLE]

Spectrophotometric Study of 8-Hydroxyquinaldine Chelates. Notes on 8-Quinolinol Chelates

By J. P. PHILLIPS AND H. P. PRICE

The soluble green complex between ferric iron and 8-hydroxyquinaldine is shown to have the same kind of structure as the corresponding 8-quinolinol complex, but no aluminum complex is formed by 8-hydroxyquinaldine. The solubilities of 8-hydroxyquinaldine and its chelates with zinc and copper were determined and the solubility products of the chelates computed. A comparison with the solubility products of 8-quinolinol chelates and of metal hydroxides demonstrates that the chelates of 8-quinolinols have the same relative stabilities as the metal hydroxides.

8-Hydroxyquinaldine forms chelates like those obtained with the better known 8-quinolinol with the exception that aluminum is not precipitated with 8-hydroxyquinaldine,¹ apparently because of steric hindrance.^{2,3} This work is a quantitative study of the properties of several 8-hydroxyquinaldine-metal complexes and a further demonstration that aluminum does not react with this reagent.

Experimental

Ferric Iron Complex.—The formula of the soluble green complex between 8-hydroxyquinaldine and ferric iron was obtained by the method of continuous variations,⁴ after running the usual test to determine that only one complex was responsible for the color. Solutions of 0.02 *M* ferric nitrate and 0.02 *M* 8-hydroxyquinaldine in dilute nitric acid were mixed in varying proportions to a total volume of 20.0 ml. The pH was adjusted to 2.2 by the addition of dilute sodium hydroxide giving a final volume of 25.00 ml. A Beckman model DU spectrophotometer with 1.00 cm. silica cells was used for all spectrophotometric measurements. The results were calculated at 580 m μ , the point of maximum absorption; the same formula was also indicated at 560 and 600 m μ .

After the complex formula was determined, the intensity of its color as a function of pH was determined at 580 m μ by measuring a number of mixtures of 10.0 ml. each of the ferric nitrate and 8-hydroxyquinaldine solutions diluted to 25.00 ml. at various pH values. The complex precipitated above a pH of about 2.6.

Aluminum.—Solutions of 0.02 *M* aluminum ion and 0.02 *M* 8-hydroxyquinaldine in dilute nitric acid were mixed in varying proportions to a total volume of 20.0 ml. and diluted with a potassium acid phthalate buffer to 25.00 ml. The solutions had a pH of 4.0 as measured with a pH meter. The spectra of these mixtures from 400–700 m μ showed no maxima, and the plot of extinction against per cent. 8-hydroxyquinaldine indicated that no complex existed at this pH. Similar results were obtained at a pH of 4.3.

Solubility Measurements.—The solubilities of 8-quinolinol and 8-hydroxyquinaldine were obtained by analyzing samples of solutions saturated with the reagents after three days immersion in a constant temperature bath controlled to $\pm 0.1^\circ$. The desired temperatures were approached from both above and below with concordant results. 5.00- or 10.00-ml. portions of the saturated solutions were removed, weighed, and diluted in a volumetric flask to 25.00 ml. with 0.1 *N* hydrochloric acid. The extinctions of these solutions were measured at several wave lengths between

320 and 400 m μ and the concentrations determined by comparison with a calibration curve obtained by dissolving various weighed amounts of 8-quinolinol or 8-hydroxyquinaldine in 0.1 *N* hydrochloric acid and determining the extinction.

The solubilities of the metal chelates between 8-hydroxyquinaldine and zinc or copper were measured similarly. Saturated solutions at several different pH values were obtained by shaking the pure chelates with water containing varying amounts of dilute hydrochloric acid or sodium hydroxide and allowing equilibrium to be reached in a constant temperature bath. 5.00 or 10.00 ml. portions of the supernatant liquid were then removed and analyzed by comparing the extinction after dilution to 25.00 ml. with 0.1 *N* hydrochloric acid (in which the chelates are completely soluble) with a calibration curve obtained by dissolving weighed amounts of the pure solid chelates in 0.1 *N* acid. At the wave lengths used zinc and copper ions had no appreciable light absorption.

The 8-hydroxyquinaldine used in these experiments was prepared as previously described,¹ vacuum distilled twice and recrystallized twice from dilute ethanol. All other chemicals were reagent grade substances.

Results and Discussion

The method of continuous variations applied to the ferric iron–8-hydroxyquinaldine color (Fig. 1) showed that the green complex in nitric acid solutions has the 1:1 mole ratio to be expected by analogy with 8-quinolinol.⁵ The color is not formed below a pH of 1.4 and increases in intensity up to the point at which precipitation of an insoluble chelate begins (about pH 2.6). In hydrochloric and sulfuric acid solutions the green color was not obtained; in perchloric acid the color formed but faded rapidly. It seems probable that these effects are the result of the reducing action of 8-hydroxyquinaldine on ferric solutions.

When the same method was applied to aluminum and 8-hydroxyquinaldine, a straight line, essentially a Beer's law plot for 8-hydroxyquinaldine, was obtained (Fig. 1). It is evident that under the conditions used no soluble complex formed between aluminum and 8-hydroxyquinaldine; it had already been demonstrated^{1,2} that no insoluble complex could be obtained under conditions where one would be expected.

The solubility of 8-hydroxyquinaldine in water was determined at two temperatures and compared

(1) Merritt and Walker, *Anal. Chem.*, **16**, 387 (1944).

(2) Irving, Butler and Ring, *J. Chem. Soc.*, 1489 (1949).

(3) Phillips and Merritt, *This Journal*, **71**, 3984 (1949).

(4) Vosburgh and Cooper, *ibid.*, **63**, 437 (1941).

(5) Sandell and Spindler, *ibid.*, **71**, 3806 (1949).