Fractional crystallization of mixtures of the di-*p*-nitrobenzoates of optically active and racemic 2,3-butanediols leads to the relative loss of the optically active isomer.[11] Therefore, the high rotations of the di-*p*-nitrobenzoates of the synthetic butanediols indicate the absence of racemized butanediol in the compound showing α_D +12.4° (in substance).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Effect of Solvent on the Pinacol Rearrangement of *cis*- and *trans*-1,2-Diphenyl-1,2-Acenaphthenediols. I. Methyl and Ethyl Alcohols[1,2]

BY RONALD F. BROWN

At room temperature it has been shown that either *cis*- or *trans*-1,2-diphenyl-1,2-acenaphthenenediol reacts in methyl or ethyl alcohol solutions in the presence of sulfuric acid to give high yields of *cis*-2-methoxy- or ethoxy-1,2-diphenyl-1-acenaphthenol. At the solvent boiling point, the principal products were 1,1-dimethoxy- or diethoxy-2,2-diphenylacenaphthene, the acetals of the pinacolone, 2,2-diphenyl-1-acenaphthenone. The pinacolone was present in varying amounts along with varying amounts of the monoether. Aluminum methylate appeared to catalyze these reactions at a slow rate in accordance with the low acidity of this material as compared with the catalyst usually used. The *cis*-monoethyl ether was converted to the *cis*-monomethyl ether and the dimethoxy acetal by reaction in methyl alcohol solutions at the boiling point in the presence of sulfuric acid. The diethoxy acetal was changed into the dimethoxy acetal and at a faster rate, under identical conditions. This is offered as contributory evidence for the assignment of the acetal structure to the dialkoxy compounds. In attempts to prepare the acetal of the pinacolone, the oxime of the pinacolone was prepared. The mono- and dimethyl ethers of the *cis*-diol were made by a Williamson synthesis, and the structure of the *cis*-monoether produced in the acid-catalyzed reaction confirmed. The dimethoxy product from the acid catalyzed reaction has been shown not to be the *cis*-dimethyl ether. The *trans*-diol has been shown to be inert to the action of active metals; the hydrogen of the hydroxyl groups was replaced only by reactive soluble reagents such as lithium aluminum hydride, or the Grignard reagent. The ultraviolet absorption spectra of all the reactants and products have been reported.

A possible explanation of the effect of water on the rate of the pinacol rearrangement of *trans*-1,2-diphenyl-1,2-acenaphthenediol (It) in acetic acid as the solvent and sulfuric or *p*-toluenesulfonic acid as the catalyst, was given in a previous paper[3] on the assumption of an inversion reaction between the conjugate acid of the diol and a molecule of water to yield *cis*-1,2-diphenyl-1,2-acenaphthenediol (Ic), which could be isolated from such a reaction mixture. However, alternate modes of interaction were not excluded by the evidence presented. In order to obtain more conclusive data, a study of this reaction in various alcohols as the solvents has been made.

Since the work of Norris and Rigby[4] had shown that tertiary ethers are easily formed when a tertiary alcohol is heated under reflux with an excess of a primary alcohol in the presence of an acid, it seemed possible that ethers of pinacols would be obtained under similar conditions. Thus, Mamedov[5] was able to prepare the ethers of acetylenic pinacols in 80 to 90% yields by the interaction of the pinacol, an alcoholic solvent, and sulfuric acid as the catalyst. Nevertheless, we were able to find conditions such that rearrangement as well as etherification occurred.

Either the *cis*- or *trans*-diol when allowed to stand at room temperature in absolute methanol containing a small amount of sulfuric acid was converted into the same product during a period of three to five days. If, on the other hand, such solutions were heated under reflux for 30 minutes, a second product was obtained. The presence of small amounts of water did not affect the yields. Analysis showed that there was one methoxyl group in the first product, and two in the second product. Because only one product predominated from either Ic or It under a given set of conditions, and by analogy to the action of water in acetic acid,[3] the first product was tentatively assigned the structure of the *cis*-monomethyl ether of I (*cis*-2-methoxy-1,2-diphenyl-1-acenaphthenol, IIIc), and the second product either that of the *cis*-dimethyl ether of I (*cis*-1,2-dimethoxy-1,2-diphenylacenaphthene, IVc), or the dimethylacetal of 2,2-diphenylacenaphthenone (1,1-dimethoxy-2,2-diphenylacenaphthene, V).

In commercial anhydrous ethyl alcohol, an analogous product was obtained at room temperature, and analysis showed the presence of one ethoxyl group. However, under reflux for 30 minutes, only the pinacolone could be isolated. When the period of reflux was shortened to five minutes, there was obtained a 60% yield of II and a 25% yield of a product which contained two ethoxyl groups as shown by analysis. Again, similar configurations were assigned.

In alcohol which had been dried over magnesium, similar results were obtained except that the proportion of ketone was reduced, and it was possible to isolate some of the monoethoxy product from the reactions carried out under reflux. This disposes of the possibility that the formation of the monoethers at room temperature was due to the removal of an insoluble product.

In order to obtain unequivocal proof of the configurational assignments, it was necessary to prepare the ethers by the reaction of a metallic derivative of the pinacols with an alkylating reagent under neutral or basic conditions to avoid any complication from an acid-catalyzed rearrangement during

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[1] Part of this paper was presented before the Organic Division, American Chemical Society Meeting, New York, N. Y., September 11–15, 1944.

[2] The numbering of the acenaphthene ring system is that recommended in the Ring Index. The 1- and 2-positions correspond with the 7- and 8-positions as used previously.[3]

[3] P. D. Bartlett and R. F. Brown, THIS JOURNAL, **62**, 2927 (1940).

[4] J. F. Norris and G. W. Rigby, *ibid.*, **54**, 2088 (1932).

[5] S. Mamedov, *Trudy Biogeokhim Lab. Akad. Nauk S.S.S.R., azerbaidzhan. filial*, No. 3, 83 (1940); *Khim. Referat. Zhur.*, **4**, No. 1, 49 (1941); See *C. A.*, **37**, 1699 (1943); **38**, 1470 (1944).

any step of the synthesis or purification.[6] After many failures, the *cis*-monomethyl ether was obtained from the *cis*-diol, in 51% conversion, by allowing it to react with sodium under nitrogen in 1,2-dimethoxyethane, adding methyl iodide, and allowing the mixture to stand at room temperature for over a week. The ether prepared in this manner proved to be identical with that obtained from the acid-catalyzed reaction in methyl alcohol. In a similar manner, IIIc was converted to the *cis*-dimethyl ether in 85% yield. However, this diether was different from the product obtained from the acid-catalyzed reaction in methyl alcohol.

It was not until 1,2-dimethoxyethane was used as a solvent that it became possible to prepare the *cis*-ethers. Previously, the action of sodium on the *cis*-diol in a variety of solvents followed by treatment with methyl iodide or methyl sulfate had all been tried at various temperatures without success. Although hydrogen was evolved in most cases, no ether was ever obtained, and the *cis*-diol was recovered. The *trans*-diol under the same conditions did not seem to evolve hydrogen, and in many instances was converted largely to 1,8-dibenzoylnaphthalene (X). The ready formation of 1,8-dibenzoylnaphthalene in those cases in which air was not excluded was markedly similar to the reaction of sodium benzpinacolate with oxygen.[7] However, no color was ever noted during the formation of the pinacolates and since the *cis*-ether was identical with that formed under acidic conditions, no side reactions other than oxidation occurred due to the presence of ketyls. The use of methylmagnesium iodide or lithium aluminum hydride on the diols to form the pinacolate liberated gas in the calculated amount, but no alkylation could be achieved in the second step. Sodamide was used under a variety of conditions without success. Although the use of 1,2-dimethoxymethane as a solvent proved successful with the *cis*-diol, the *trans*-diol still proved resistant to alkylation. This inertness of the *trans*-diol or of the corresponding pinacolate ion may be ascribed to "F strain,"[8] namely, the steric difficulty of a molecule, ion, or surface being brought within bond formation distance of the hydroxyl group in the *trans*-diol or of the negatively charged oxygen in the ion. The hydroxyl groups, as illustrated by Fisher–Hirschfelder models, are at the bottom of a shallow valley, surrounded by the bulky phenyl and naphthyl groups which act as barriers to the formation of a transition state on the oxygen atom unless the entering reactant of a small enough size approaches within closely defined limits.

Since the *trans*-ethers could not be prepared, it became necessary to prepare the acetals, V and VIII of II. Unfortunately, however, it has been impossible to convert the pinacolone into any acetal by an independent means. Treatment of the pinacolone with ethyl orthoformate under a variety of conditions led only to the recovery of starting material. Treatment of the pinacolone with phosphorus pentachloride followed by methyl or ethyl alcohols also was unsuccessful. It had been hoped that the oxime would undergo alcoholysis to yield an acetal, but the oxime was recovered unchanged from solution after an eight-day period of heating under reflux in absolute methanol with sulfuric acid.

The use of aluminum methylate in methanol as an acidic catalyst[9] was disappointing in that it was necessary to use a large excess of the catalyst and prolonged periods of heating under reflux in order to obtain any reaction. Either diol could be converted by this method in the course of nine days into II, in 25% yield, IIIc in 6% yield, and V in 38% yield. However, such results indicated the possibility of pinacol rearrangements in the aluminum alcoholate reductions of α-halo-,[10] α-amino- or α-hydroxyketones, especially if the reaction time was prolonged.

Any one of the ethers or acetals was converted quantitatively into the pinacolone by heating for a few minutes in acetic acid to which a few drops of sulfuric acid had been added. Moreover, the monoethyl ether could be converted into a mixture which consisted of a large amount of monomethyl ether and a small amount of dimethyl acetal by reaction in methyl alcohol at the boiling point in the presence of sulfuric acid. On the other hand, the diethyl acetal under similar treatment was converted more rapidly and solely to dimethyl acetal, no trace of a mixed alkoxy compound or of the monoether being found. This additional evidence was consistent with the assignment of an acetal structure to the dialkoxy compounds since any ether assignment would make likely the formation of some mixed diether as well as some monoether in such an interchange of groups. This seems to be the strongest evidence available for the assignment of the acetal instead of *trans*-diether configuration.

In the absence of infrared equipment, the ultraviolet absorption spectra of all the substances involved was determined in the hope that some feature of the absorption curves would furnish additional information, but the results as given in Fig. 1 do not provide evidence for a decision. The curves are very similar in appearance to that of acenaphthene[11] except for that of the pinacolone, which is similar to that for 5-acetoacenaphthene, wherein the C-effect is pronounced. If anything, there is a slight hypsochromic effect for the diols, ethers and acetals as compared to acenaphthene along with some loss of fine structure.

A discussion of the theoretical implications of the

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(6) A reverse synthesis using the pinacolic chlorides such as *cis*- or *trans*-1,2-dichloro-1,2-diphenylacenaphthene with metal alkoxides cannot be utilized since the structures of the halides are unknown. We are in process of studying these substances.

(7) W. E. Bachmann, THIS JOURNAL, **55**, 1179 (1933); R. N. Doescher and G. W. Wheland, *ibid.*, **56**, 2011 (1934); S. Sugden, *Trans. Faraday Soc.*, **30**, 18 (1934); F. L. Allen and S. Sugden, *J. Chem. Soc.*, 440 (1936). See also G. W. Wheland, "Advanced Organic Chemistry," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 716–720; and W. E. Bachmann in H. Gilman, "Organic Chemistry," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 612–613.

(8) H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, THIS JOURNAL, **66**, 435 (1944).

(9) H. Meerwein, *Ann.*, **455**, 227 (1927).

(10) P. G. Stevens, THIS JOURNAL, **60**, 3089 (1937); S. Winstein, *ibid.*, **61**, 1610 (1939); P. G. Stevens and O. C. W. Allenby, *ibid.*, **62**, 3264 (1940).

(11) R. N. Jones, *ibid.*, **67**, 2127 (1945).

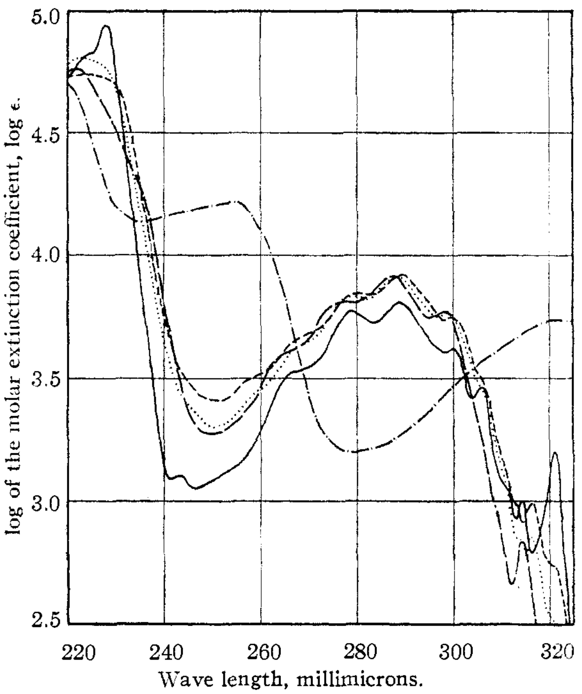


Fig. 1.—Absorption spectra in 95% ethanol of: ——, acenaphthene; · · · · · · ·, *trans*-1,2-diphenyl-1,2-acenaphthenediol (It); - - - - - - -, *cis*-1,2-diphenyl-1,2-acenaphthenediol (Ic). The spectra of the monomethyl ether (IIIc), the dimethyl ether (IVc) and the monoethyl ether (VIc) are practically identical with that of *cis*-diol; — - — -, 2,2-diphenyl-1-acenaphthenone (II); — —, 1,1-dimethoxy-2,2-diphenylacenaphthene (V), an acetal of II. The spectrum of the diethyl acetal ether (IIIc), VIII, is identical within experimental error.

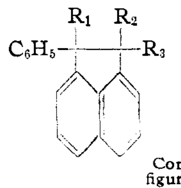
reactions reported will appear in the next paper in this series.

Experimental[12]

cis- and *trans*-1,2-diphenyl-1,2-acenaphthenediols were prepared as described previously.[3] All solvents and reagents used were of ordinary quality, unless noted otherwise. Physical properties of the products are summarized in Table II.

TABLE I

COMPOUNDS AND PRODUCTS



No.	R1	R2	R3	Configuration[a]	Trivial name
I	OH	OH	C_6H_5	*c* or *t*	Diol
III	OH	OCH_3	C_6H_5	*c* or *t*	Monomethyl ether
IV	OCH_3	OCH_3	C_6H_5	*c* or *t*	Dimethyl ether
V	C_6H_5	OCH_3	OCH_3	..	Dimethyl acetal
VI	OH	OC_2H_5	C_6H_5	*c* or *t*	Monoethyl ether
VII	OC_2H_5	OC_2H_5	C_6H_5	*c* or *t*	Diethyl ether
VIII	C_6H_5	OC_2H_5	OC_2H_5	..	Diethyl acetal
II	C_6H_5	=O		..	Ketone or pinacolone
IX	C_6H_5	=NOH		..	Oxime

[a] *c* for *cis*-, and *t* for *trans*-, refer to the relative positions of the phenyl groups about the five-membered ring.

The general procedure followed was to add a weighed amount of the diol (usually 1.7 g. (0.005 mole)) to a given volume of the solvent, concentrated sulfuric acid added dropwise with stirring, and the reaction mixture allowed to stand at room temperature or heated rapidly to boiling under reflux. The reaction was terminated by pouring the reaction mixture into a dilute solution of sodium hydroxide, with stirring to hasten coagulation. The product was filtered, washed thoroughly with water, dried and recrystallized. In those room temperature runs during which the product crystallized, the solution was decanted and the crystalline residue was digested with dilute sodium hydroxide, filtered, washed, dried and recrystallized.

Reactions at Room Temperature.—*cis*- or *trans*-diol, 5 g., in 100 ml. of methanol, with 1 ml. of sulfuric acid, in 18 hours yielded 2.5 g. of IIIc, m.p. 187–190°; at the end of three days, 2.0 g., m.p. 188–190°; and on the twelfth day, V, 0.3 g., m.p. 192.5–194.5°, shown to be different from the first two fractions by a mixed melting point determination. A fourth fraction, 0.1 g., m.p. 192.5–195.0°, was obtained by concentrating the reaction mixture. Recrystallization from methyl cellosolve or Skelly C gave pure materials.

cis- or *trans*-diol, 1.0 g., in 30 ml. of commercial anhydrous ethanol, with 2.0 ml. of catalyst, in three days yielded 1.0 g. of VIc, m.p. 173–174°. Recrystallization from ethanol or Skelly C gave a pure product which has two crystalline modifications, prisms or needles, the latter changing over to prisms on standing. A mixture of the two forms has the same melting point as the pure prisms, 176.5–177.5°.

Reactions at the Boiling Point.—*cis*- or *trans*-diol, 1.7 g., in 150 ml. of methanol, with 3 drops of catalyst (0.05 ml.) heated under reflux for 30 minutes, and the product crystallized from benzene, Skelly C, or methanol gave 1.6 g. of pure V, m.p. 195–196°.

cis- or *trans*-diol, 1.0 g., in 15 ml. of commercial anhydrous ethanol, with 1.0 ml. of catalyst, heated under reflux for 30 minutes, and crystallized from ethanol or Skelly C gave 1.0 g. of II, m.p. 174–175°, checked by a mixed melting point with an authentic sample. Heated for only five minutes, 0.65 g. of the pinacolone, and 0.20 g. of VIII, m.p. 140–141°, prisms, were obtained.

cis-Diol, 0.25 g., in 20 ml. of anhydrous ethanol dried over magnesium and distilled directly into the reaction flask, heated under reflux for one minute with 3 drops of catalyst, after crystallization, yielded 0.10 g. of the monoethoxy compound, and 0.10 g. of recovered *cis*-diol. Heated under reflux for five minutes, 0.50 g. of the *cis*-diol gave 0.32 g. of the monoethyl ether, and traces of *cis*-diol, diethyl acetal and pinacolone. Heated under reflux for 20 minutes, 1.0 g. of *cis*- or *trans*-diol, or monoethyl ether, 35 ml. of anhydrous ethanol, 5 drops of catalyst gave 0.65 g. of monoethyl ether, 0.05 g. of diethyl acetal, VIII, 0.05 g. of pinacolone and considerable oily residue. Heated under reflux for one hour with 10 drops of catalyst, there was obtained 0.1 g. of VIc, 0.40 g. of VIII, 0.3 g. of II, and 0.15 g. of oily residue.

Monoethyl ether, 0.25 g., in 50 ml. of magnesium-dried methanol heated under reflux for 30 minutes with 5 drops of catalyst, yielded 0.15 g. of IIIc, 0.02 g. of V, and 0.05 g. of oily residue. Repetition with diethyl acetal gave 0.20 g. of V, and 0.04 g. of oily residue. Thus the acetal reacts much more quickly than the monoether. Non-identity was shown in every case by a large depression (20 to 40°) in the melting point of mixtures.

Aluminum Methylate as a Catalyst.—Magnesium-dried methanol, 160 ml., 2.7 g. (0.1 mole) of aluminum turnings, and *cis*- or *trans*-diol, 1.7 g. (0.005 mole), was heated under reflux for nine days, terminated in the usual manner, and the product crystallized from isopropyl alcohol to give 0.8 g. of the monomethyl ether, 0.4 g. of the starting material, and 0.1 g. of V.

Conversion to Pinacolone.—Any one of the ethers or acetals was changed into the pinacolone in better than 95% yield when treated with a few drops of concentrated sulfuric acid in boiling glacial acetic acid solution for 10 to 15 minutes.

Preparation of *cis*-Ethers.—1,2-Dimethoxyethane was prepared by a Williamson synthesis from methyl cellosolve (2-methoxyethanol), fractionated and dried by prolonged heating under reflux with sodium. The solvent was distilled, b.p. 85.0–85.1°, over sodium and under nitrogen into flask which contained 3.4 g. (0.01 mole) of the *cis*-diol, and

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[12] All melting points are uncorrected.

TABLE II

PHYSICAL DATA FOR PRODUCTS

			Analyses, %					
			Calculated			Found		
Compd.	M.p., °C.	Formula	C	H	RO	C	H	RO
IIIc	191.0–191.6	$C_{25}H_{20}O_2$	85.20	5.72	8.80	85.03	5.73	8.79[a]
IVc	156.5–157.5	$C_{26}H_{22}O_2$	85.22	6.05	16.94	85.16	6.10	16.82[b]
V	197.2–197.6	$C_{26}H_{22}O_2$	85.22	6.05	16.94	85.22	5.91	16.71[a]
VIc	176.5–177.5	$C_{26}H_{22}O_2$	85.22	6.05	12.30	85.23	6.12	12.21[b]
VIII	140.0–141.0	$C_{28}H_{26}O_2$	85.24	6.64	22.84	85.25	6.60	22.74[b]
IX	235–236	$C_{24}H_{17}ON$	85.94	5.11	4.18[c]	85.87	5.22	4.27[c,a]

[a] Analyses by Microchemical Laboratory, California Institute of Technology, Professor A. J. Haagen-Smit, Director. [b] Analyses by Elek Micro Analytical Laboratories, Los Angeles 16, California. [c] Data for nitrogen, not alkoxy.

0.25 g. (0.011 g. atom) of sodium until approximately 50 ml. had been collected. The solvent was brought to a boil under reflux and the system swept with nitrogen for ten minutes and then allowed to remain under an atmosphere of nitrogen. Although some of the sodium remained undissolved at the end of five hours of heating, the mixture was cooled, 2.9 g. (0.02 mole) of methyl iodide was added, and the system allowed to stand at room temperature for one week. An equal volume of ethyl ether was added, the solution washed with successive small portions of sodium bisulfite solution and sodium hydroxide solution, dried over sodium sulfate and the solvent removed by distillation. The final residue crystallized from Skelly C gave 1.8 g. (51% conversion) of IIIc, melting at 189–190°, and 1.0 g. of *cis*-diol. The product was identical with that obtained in the room temperature runs in methanol as a solvent, as shown by a melting point of a mixture with an analytical sample, m.p. 190.5–191.5°, of 190–191°.

The *cis*-dimethyl ether was prepared as above, using 1.8 g. (0.005 mole) of IIIc, which gave 1.55 g. of crude or 1.35 g. (75% conversion) of pure *cis*-1,2-dimethoxy-1,2-diphenylacenaphthene (IVc), m.p. 156–157.5°. This substance occurs as prisms or needles, interconvertible in Skelly C solution, the former being favored by slow cooling. When mixed with the dimethoxy compound, m.p. 197.2–197.6°, obtained under rearrangement conditions, the mixture melted at 141–167°; with *trans*-diol of m.p. 156.0–156.5°, the mixture melted at 130–149°.

trans-Diol, treated in the same manner, did not react with the sodium, and over 95% of the material was recovered except for a trace of 1,8-dibenzoylnaphthalene (X). The pinacolate was prepared by the use of lithium aluminum hydride, hydrogen was evolved, but again, *trans*-diol was recovered in better than 90% of the calculated amount.

Attempted Preparation of Pinacolone Acetals.—Pinacolone, 5.0 g., heated under reflux in 150 ml. of anhydrous methanol with 1.5 ml. of sulfuric acid for one week led to the recovery of 4.9 g. of the ketone.

Pinacolone, 2.0 g., and hydroxylamine hydrochloride, 2.0 g., was heated under reflux in a mixture of 10 ml. of anhydrous ethanol and 10 ml. of pyridine for a period of four days. Water was added until the solution became cloudy, and on cooling, 1.0 g. of pinacolone which crystallized was filtered. The filtrate was poured into an excess of water, the mixture allowed to stand one day to coagulate, and the product collected. When dry, the material was extracted with two portions of Skelly C at the boiling point to remove an additional 0.4 g. of the pinacolone. The residue was crystallized from methyl cellosolve to give 0.5 g. of the oxime, IX, tan glistening rods the ends of which show red, m.p. 228–232°. Impure samples melt with decomposition. The sodium hydroxide method for the preparation of the oxime leads to the formation of 8-diphenylmethylnaphthoic acid,[8] m.p. 231–232°, as the only isolatable product.

The oxime, 0.6 g., was heated for three days under reflux in 75 ml. of glacial acetic acid with 1 ml. of water and 2 ml. of sulfuric acid, and the product isolated by pouring into water. The product, 0.6 g., melted at 222–225°, and mixed with the oxime, at 226–232°. Oxime, 0.75 g., was heated under reflux in 150 ml. of anhydrous methanol with 2 ml. of sulfuric acid for eight days and the product isolated in the usual manner. The recovered material, 0.70 g., m.p. 214–226°, when mixed with oxime melted at 225–231°.

Many attempts were made to prepare the acetal by allowing the pinacolone and phosphorus pentachloride to interact either alone or in carbon tetrachloride or chlorobenzene solution, at room temperature, or up to 150°, for varying lengths of time up to one day, followed by treatment with methanol. In no case could anything be isolated except the pinacolone in amounts up to 90% recovery.

Attempts to prepare an acetal by means of the orthoester method also failed. The pinacolone was allowed to stand in various mixtures of orthoformic ester and absolute ethanol with various catalysts, such as ammonium chloride, hydrogen chloride, and sulfuric acid, at temperatures from room temperature up to 90°, for periods up to two weeks. In every case, the pinacolone was recovered pure in over 95% of the calculated amount.

Ultraviolet absorption spectra of all substances mentioned were determined in 95% ethanolic solution in a Beckman spectrophotometer, model DU. Concentrations used were of the order of 0.00001 molar. The results are given in Fig. 1.

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