[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. II. Isopropyl and *t*-Butyl Alcohols[1,2]

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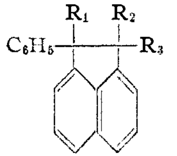
It has been shown that either *cis*- or *trans*-1,2-diphenyl-1,2-acenaphthenediol reacts in isopropyl alcohol solutions in the presence of sulfuric acid at room temperature to give high yields of *cis*-2-isopropoxy-1,2-diphenyl-1-acenaphthenol, while at the boiling point the pinacol rearrangement product, 2,2-diphenyl-1-acenaphthenone, is the sole product. Acetic acid as a catalyst is without effect at room temperature but at the temperature of heating under reflux, the *cis*-isopropyl ether is formed slowly. In tertiary butyl alcohol as a solvent, no participation in the rearrangement reaction occurred and the *trans*-diol yielded mixtures of starting material, *cis*-diol, and pinacolone. The rates of these reactions were measured in a rough qualitative manner. A mechanism is proposed and discussed for these reactions and those reported in the previous paper in which a carbonium ion is suggested as a relatively stable intermediate.

Since the first paper in this series[3] reported the participation of primary alcoholic solvents in the reactions of *cis*- and *trans*-1,2-diphenyl-1,2-acenaphthenediols (Ic and It), under acid catalysis which would normally lead to the formation of a pinacolone, 2,2-diphenyl-1-acenaphthenone (II), we decided to extend the study to include the effects of typical secondary and tertiary alcohols, namely, isopropyl and *t*-butyl alcohols. Such changes in the solvent-medium would have several effects, the most important of which for our purpose would be the increasing steric difficulty of the more branched alcohols in participating in the reaction to form ethers and acetals. In fact, one would expect *t*-butyl alcohol to form neither an ether nor an acetal, and this was found to be true.

All of these reactions were carried out at room temperature or at the boiling point of the solvent by dissolving one gram of the reactant in 100 ml. of solvent with four drops of catalyst. In a few cases the rates were determined in a very rough manner by interrupting the reactions at appropriate intervals by pouring the solutions into an excess of water and determining the composition of the precipitated product by fractional crystallization. The results obtained are given in Table II.

Table I

Compounds and Products



No.	R_1	R_2	R_3	Configuration[a]	Trivial name
I	OH	OH	C_6H_5	*c* or *t*	Diol
XI	OH	$OCH(CH_3)_2$	C_6H_5	*c* or *t*	Monoisopropyl ether
XII	C_6H_5	$OCH(CH_3)_2$	C_6H_5	*c* or *t*	Diisopropyl ether
XIII	C_6H_5	$OCH(CH_3)_2$	$OCH(CH_3)_2$	...	Diisopropyl acetal
II	C_6H_5	$=O$		...	Ketone or pinacolone

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

Table II

Products Formed

Reactant	Solvent[a]	Catalyst	Temp., °C.	Time	Products	Yield %
cis-Diol	P	H_2SO_4	25	3 days	Ether	44
				4 days	Ether	57
				5 days	Ether	71
				14 days	Ether	100
			81	15 min.	Ketone	100
		HOAc	25	7 days	No reaction	...
			81	56 hrs.	Ether	100
		None	81	1 wk.	No reaction	...
	B	H_2SO_4	25	9 days	Ketone	33
			83	2 hrs.	Ketone	11
				4 hrs.	Ketone	34
				12 hrs.	Ketone	90
trans-Diol	P	H_2SO_4	25	5 days	*cis*-Diol, ether	...
			81	30 min.	*cis*-Diol, ether, ketone	...
				75 min.	Ketone	100
		HOAc	25	7 days	No reaction	...
			81	24 hrs.	No reaction	...
	B	H_2SO_4	25	14 days	Ketone	34
			83	12 hrs.	Ketone	2
					trans-Diol	78
				16 hrs.	Ketone	8
					trans-Diol	49
				24 hrs.	Ketone	45
					cis-Diol	12
				2 days	Ketone	65
					cis-Diol	28
				3 days	Ketone	96
Ether (XIc)	P	H_2SO_4	25	7 days	No reaction	...
			81	15 min.	Ketone	16
				30 min.	Ketone	48
				60 min.	Ketone	100
		HOAc	81	12 hrs.	No reaction	...

[a] P refers to absolute isopropyl alcohol; B to *t*-butyl alcohol.

In isopropyl alcohol, the *cis*-diol, with sulfuric acid as the catalyst, at room temperature was slowly converted into *cis*-2-isopropoxy-1,2-diphenyl-1-acenaphthenol (XIc). The configuration was assumed on the basis of the similar result obtained in methanol as the solvent and in which the configuration was proved by an independent synthesis.[3] At the boiling point of the solvent, Ic was converted to the pinacolone in quantitative yield in the course of 15 minutes. On the other hand, XIc was unaffected in seven days at room temperature, was much more slowly changed into II at the boiling point, and was not an intermediate in the rearrangement of Ic to II. With acetic acid as the catalyst, the results confirmed those obtained by the use of sulfuric acid as the catalyst in that the *cis*-diol reacted more rapidly under a given set of conditions than did the isopropyl ether to form II.

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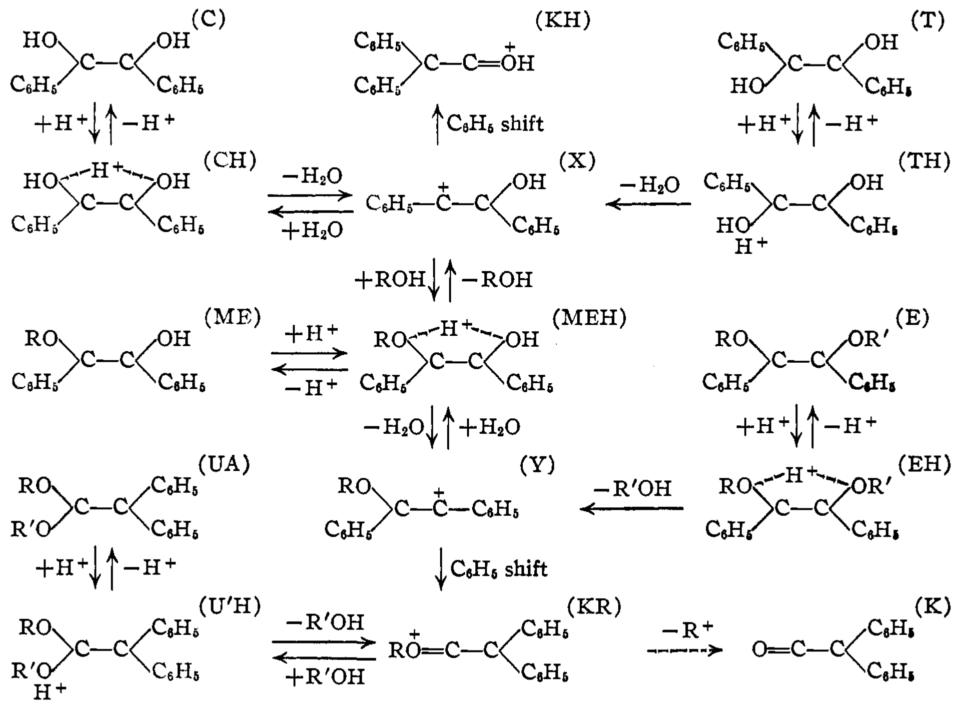
[1] Parts of this paper are abstracted from the theses of Joseph B. Nordmann and of Milton Madoff presented to the Faculty of the Department of Chemistry of the University of Southern California in partial fulfillment of the requirements for the Degree of Master of Science in Chemistry, October, 1945, and February, 1946.

[2] Part of this paper was presented before the Organic Division, American Chemical Society Meeting, Chicago, Ill., September 3-8, 1950.

[3] R. F. Brown, This Journal, **73**, 428 (1951).



(In these formulas, the acenaphthene ring system is envisioned as projecting downward from the plane of the paper.)

The *trans*-diol at room temperature with sulfuric acid as the catalyst also gave only the same isopropyl ether when allowed to stand for two weeks. At the end of a five-day period, however, not only could the ether be isolated, along with some unreacted *trans*-diol, but also some of the *cis*-diol. In this respect, the isolation of the *cis*-diol was similar to the results obtained when acetic acid was used as the solvent.[4] At the boiling point, the reaction again was more complex than the *cis*-diol in that after 30 minutes *cis*- and *trans*-diols, the ether and pinacolone were isolated. Yet after a 75-minute period of heating, only the pinacolone was isolated in almost quantitative yield. Thus the reaction of the *trans*-diol in isopropyl alcohol, as in acetic acid, was somewhat slower than was that of the *cis*-diol. Again, similar results were obtained using acetic acid as the catalyst, namely, no reaction over a period of one week at room temperature, and no reaction over a period of one day at the boiling point.

In comparing these results with those obtained in methyl and ethyl alcohols, the most striking difference encountered was the lack of formation of a diisopropoxy compound, either the diether, XII, or the acetal, XIII. Presumably, this was because of the difficulty of crowding two isopropoxy groups into the *cis* position as in XIIc in the case of a diether, or onto one carbon as in the case of the acetal. The failure to obtain an acetal was a continuation of the trend noted with methyl and ethyl alcohols, the former forming an acetal in almost quantitative yield, the latter forming an acetal under carefully controlled conditions and then mixed with pinacolone and monoether in every instance.

In tertiary butyl alcohol, the reactions proceeded as expected, no ethers or acetals were isolated in any instance, and the rates were the slowest of any solvent studied. It required 12 hours at the boiling point of the solvent to obtain a 90% conversion to the pinacolone if *cis*-diol were the reactant, and three days if *trans*-diol were the reactant. At room temperature, the reaction was correspondingly slower, and in the case of the *trans*-diol isomerization to *cis*-diol as well as rearrangement occurred.

Many futile attempts were made to synthesize the monoisopropyl ether from the *cis*-diol in order to prove the *cis*- configuration. The assignment is based on the analogous proof of structure of the methyl ethers. Also many attempts were made to prepare the acetates of the diols, all without success, in order to study the possible role of such esters in the reactions carried out in acetic acid as the solvent.

Discussion

It will be convenient to present our proposed mechanism directly. In acetic acid as the solvent, C equilibrates through CH with X, and the rate step may be that of the shift of the phenyl group or of any of the preceding steps leading to first order kinetics. As water is formed during the reaction, the equilibrium between CH and X will be shifted somewhat toward CH causing a slight decrease in the rate as is observed. At higher initial concentrations of water, the effective concentration of X will be lowered not only by the equilibrium shift involving X, but the net acidity of the system is lowered and the equilibrium between C and CH is shifted toward C. *trans*-Diol in equilibrating with TH is affected by the concentration of water only by way of the effect on the acidity of the system, and the irreversible dehydration step to form X is not affected at all in terms of specific rate. At high concentrations of water, X will coördinate with water and form CH and C at a rate faster than X rearranges,

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

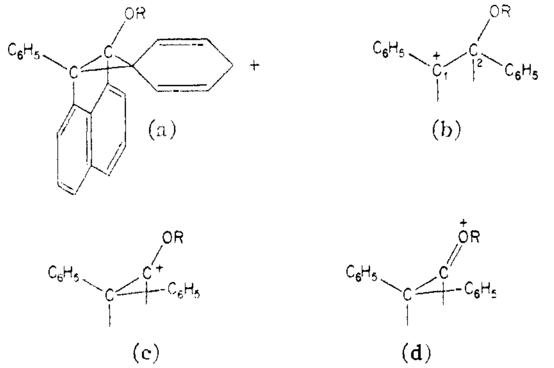
causing *cis*-diol to accumulate. By the use of space models, it is seen that in X, even though planar about the positive carbon, the phenyl group on the adjacent carbon hinders the approach to the positive carbon more than does the hydroxyl group on the opposite side of the plane. Thus, coördination with the ion leads to a *cis*-configuration. The ion, X, once formed, may coördinate with water or rearrange by a shift of a phenyl group to form the conjugate acid, KH, of the pinacolone. It seems reasonable to suppose that the concentration of X will rise from an initially low value to a maximum as the concentration of CH and C increases and as T decreases, and is thereafter dependent on C. It is necessary to assume that acetic acid is such a poor base that coördination with X to form acetates occurs only to a very minor extent, if at all, since no trace of one was ever found.

If the reaction is carried out in an alcohol as a solvent, there will be competition with any water present for reaction with X, depending upon the relative basicities, structures and concentrations to give MEH or CH. It is not surprising that methyl alcohol is capable of excluding small amounts of water from reacting with X, ethyl alcohol being somewhat less efficient, isopropyl alcohol still less so, and *t*-butyl alcohol unable to compete at all. If methyl alcohol is the solvent at room temperature, MEH merely loses a proton to an acceptor in the system, the reaction of MEH to Y occurring to a very slight extent. At the boiling point, however, MEH does equilibrate with the ion, Y, which should be capable of equilibrating through EH to form the *cis*-dimethyl ether, E (R and R′ = CH_3). However, the front face of the ion is hindered more than in X because now instead of a hydroxy group there is the much bulkier methoxy group to be pushed aside by an incoming molecule of alcohol. Such being the case, the phenyl group shifts, KR is formed, and an acetal is the end product. The results were essentially the same as would be expected in the other alcohols at room temperature, but at the boiling point, K became increasingly important as a product. Presumably this is due to the increasing difficulty of formation of MEH from X, which allows the rearrangement of X to KH to occur more readily.

If one allows any of the monoethers to react in acetic acid with sulfuric acid catalyst, ME goes to either X or Y and on to K. The only *cis*-diether available, the dimethyl, as E, goes to Y and thence to K through KR, or to K through X. It would seem that the path to X to KH to K is the preferred one, although it still remains possible for Y to go to KR which could coördinate with water and thence to K by proton interchange and loss of methyl alcohol. If, however, the monoethyl or monoisopropyl ethers, Me with R = Et or *i*-Pr, are allowed to react in methyl alcohol at the boiling point with the usual catalyst, the major product is monomethyl ether along with some dimethyl acetal. The monomethyl ether arises only through MEH and X, the latter coördinating with solvent methyl alcohol returning through MEH to ME. If the major path from MEH were through Y, then the major product would have been the dimethyl acetal, since in the absence of water, Y could only go to KR, and thence to UA, the unsymmetrical acetal, which in the presence of acid and methyl alcohol would rapidly be converted to the symmetrical dimethyl acetal. Furthermore, with R = *i*-Pr, one might expect some of the KR to go directly to K, a product which was not observed. Therefore, MEH reacts almost exclusively to give X rather than Y, and a reaction may be forced to go through Y to KR only when the path to X is almost blocked by the use of an alcohol which shifts the equilibrium between X and MEH far over toward MEH, as is the case when methyl alcohol and, to a much lesser extent, ethyl alcohol is used as a solvent.

The view that the departure of a water molecule and the migration of a group from the back side occur simultaneously[5] is not applicable in the present instance, for obvious reasons.

If the formulation of X and Y as carbocyclic ions (or π-complexes) is adopted, four structures may be considered as contributing to πX and πY,



(a) (b) (c) (d)

πX, R = H πY, R = Me, Et or *i*-Pr

of which, unlike the more symmetrical complexes involved in the Wagner–Meerwein rearrangement,[6] one is the ketone-like structure, (d). Any contribution of this form will increase the bonding of the migratory group to C_1 over that to C_2, and there does not seem to be sufficient reason to expect much of an energy barrier to the completion of the shift. If this is the case, the π-complex would not exist as an intermediate, and the transition state for migration would occur before the migrating group reaches the mid-point of the traverse.[7] It is interesting to note that πX would have to react at C_1 to give *cis*-monoethers whereas πY would have to react at C_2 to yield acetals. As R is varied from H to Me to Et, etc., (d) should become a more important contributing form and reaction at C_2 would be increasingly favored. However, it is difficult to account for the high

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(5) G. W. Wheland, "Advanced Organic Chemistry," Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 534; G. H. Stempel, Jr., *J. Chem. Education*, **23**, 434 (1946).

(6) S. Winstein and D. S. Trifan, This Journal, **71**, 2453 (1949); D. J. Cram, *ibid.*, **71**, 3863 (1949); J. D. Roberts, R. E. McMahon and J. S. Hine, *ibid.*, **72**, 4237 (1950).

(7) See M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, pp. 207–218, for another point of view, specially p. 213 and p. 215.

specificity for reaction at C_1 in πX by this scheme.[8] If an explanation is sought in terms of the geometry of the system, it would seem that the influence of (d) would favor a coplanar arrangement of the groups except for the migratory phenyl. But in view of the bond stretching stress between C_1 and C_2 due to the acenaphthene ring system, the *p*-orbital overlap would be weakened and cyclopropanoid geometry would be favored in the π-complex. These opposing tendencies are difficult to evaluate, although the latter is probably predominant. In any case, as R is increased in size, reaction at C_1 would be favored, but less so if ethylenic geometry was the determinant. On the other hand, the use of the carbonium ion formulation offers both steric and electronic explanations for the results obtained.[9] Finally, it is impossible for TH to go directly to πX. A reasonable path is *via* X. Then if the postulate is made that the activation energy for the conversion of TH to X is greater than for CH directly to πX, the slower rate of rearrangement of T than C in acetic acid of low water content is explained. Alternately, if one prefers the carbonium ion formulation, it is necessary to postulate that the equilibrium $\mathrm{T} \rightleftarrows \mathrm{TH}$ is not so far to the right as is $\mathrm{C} \rightleftarrows \mathrm{CH}$ because of the "F-strain" already discussed.[3]

The evidence is admittedly inconclusive, but the formulation of X and Y as ions rather than as π-complexes seems to offer a more coherent picture for the interpretation of these reactions.

Experimental[10]

Reagents.—Commercial isopropyl alcohol was heated under reflux with an excess of aluminum isopropylate and distilled as needed, b.p. 80.5–81.5°. A good grade of commercial *t*-butyl alcohol was heated under reflux with an excess of aluminum *t*-butylate and distilled as needed, b.p. 82.0–83.5°.

Sulfuric acid, 100%, was prepared by adding the calculated amount of 30% fuming sulfuric acid to concentrated C.P. 94.5–96.5% sulfuric acid. Acetic acid, 100%, was prepared by adding the calculated amount of acetic anhydride to glacial C.P. acetic acid, 99%.

cis- and *trans*-1,2-diphenyl-1,2-acenaphthenediols were prepared as described previously.[5]

Procedure.—The reactant, 1.0 g., approximately 0.003 mole for the diols, slightly less for the ethers, was dissolved in 100 ml. of freshly distilled solvent and four drops of anhydrous sulfuric or acetic acid added to start the reaction. The reaction rates were measured in very rough manner by pouring the solution into an excess of water, which precipitated the products and remaining reactant. After filtering, washing thoroughly with water, and drying, the solid material was recrystallized from the appropriate solvent until the pure components could be identified by melting point determination and determination of the melting point of a mixture with an authentic sample. Total recovery of crude solid material was in excess of 95% in every case, but the attendant separation into the components was always accompanied by unavoidable losses. The results are tabulated in Table II.

cis-2-Isopropoxy-1,2-diphenyl-1-acenaphthenol (XIc) was prepared by heating under reflux 1.0 g. of *cis*-diol with four drops of anhydrous acetic acid and 100 ml. of anhydrous isopropyl alcohol for three days. The solution was poured into an excess of water, and the product isolated as described above. Crystallization from isopropyl alcohol gave 0.92 g., 87% yield, of pure material, colorless prisms, m.p. 202.4–203.0°. The product may also be obtained by allowing similar solutions of either the *cis*- or *trans*-diol with sulfuric acid as the catalyst to stand at room temperature for two weeks, during which period the ether will crystallize from the solution in practically quantitative yield.

Anal. Calcd. for $C_{27}H_{24}O_2$: C, 85.23; H, 6.36; active hydrogen, 1.00. Found: C, 84.97; H, 6.52[11]; active hydrogen, 1.05.[12]

The ultraviolet absorption spectrum was identical with other *cis*-ethers in this series.[3]

Many attempts to synthesize XIc were made, all ending in failure. One method used was to add either diol to a solution of sodamide in liquid ammonia, allow the solvent to evaporate, and add a variety of solvents (such as benzene, ether, petroleum ether, etc.) with the calculated amount of isopropyl bromide. The mixture was then kept at various temperatures (from −80 to 80°) for various lengths of time. The only product isolated other than starting material was 1,8-dibenzoylnaphthalene in yields up to 90%. Heating the magnesium pinacolate of the *cis*-diol (obtained by means of a Gomberg–Bachmann reduction[13] of 1,8-dibenzoylnaphthalene[4]) with isopropyl bromide gave only a small quantity of *cis*-diol.

The *cis*-isopropyl ether, 0.28 g., when treated in 50 ml. of absolute methyl alcohol with 5 drops of sulfuric acid and heated under reflux for 30 minutes, the product isolated in the usual manner gave 0.18 g. (69% yield) of *cis*-monomethyl ether,[3] m.p. 190–192°, mixed with a sample of m.p. 191–192° gave m.p. 190–192° and 0.05 g. (19% yield) of the dimethyl acetal, m.p. 193–194°, mixed with a sample of m.p. 195–196°, gave m.p. 194–195.5°.

All attempts to prepare the acetates of *cis*- or *trans*-diol failed, only starting material and varying amounts of the pinacolone being recovered. The following acylating mixtures at room temperature or temperatures of heating under reflux were tried: diol and acetic acid with added acetic anhydride, diol and acetic anhydride, diol and acetic anhydride or acetyl chloride in the presence of pyridine, magnesium pinacolates and acetic anhydride or acetyl chloride.

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[8] This line of reasoning is based on the tacit assumption that reactivity is a function of the relative contributions of the written structures to the hybrid and, of course, is not necessarily true. It is mentioned only to indicate a few of the factors necessary to an adequate explanation of the data.

[9] It should be pointed out that the ion might be destabilized somewhat by the deformation of the bond angles of the bond to the naphthalene ring, which might disfavor those structures by which the charge is dispersed into the naphthalene system.

[10] All melting points are uncorrected.

[11] Analysis by Microchemical Laboratory, California Institute of Technology, Professor A. J. Haagen-Smit, Director.

[12] Analysis by the Department of Chemistry, University of California at Los Angeles.

[13] M. Gomberg and W. E. Bachmann, THIS JOURNAL, **49**, 236, 2584 (1927).