had m.p. 197-199°, $[\alpha]^{30}\mathrm{D}$ $-21.73°$ (*c* 3.50 in methanol, *l* 4). Recrystallization gave material of m.p. 198.5-199°, $[\alpha]^{30}\mathrm{D}$ $-21.65°$.

Anal. Calcd. for $C_{20}H_{14}O$: C, 88.89; H, 5.19. Found: For (−)-isomer: C, 88.88; H, 5.21. For (+)-isomer: C, 88.76; H, 5.33.

Racemization Experiments. A. Acid Succinate.—A solution of 0.75 g. of the acid succinate, $[\alpha]^{30}\mathrm{D}$ $-37.45°$, in 25 ml. of benzene was heated at reflux for 24 hours. The benzene was evaporated *in vacuo*, leaving 0.70 g. of material, m.p. 237-239°, $[\alpha]^{29.6}\mathrm{D}$ $-35.61°$ (4.9% racemization).

B. **2-Hydroxy-1,1'-binaphthyl in Benzene.**—A solution of 0.50 g. of I, $[\alpha]^{30}\mathrm{D}$ $+21.70°$, in 25 ml. of benzene was heated at reflux for 24 hours. The benzene was removed *in vacuo* leaving 0.47 g. of material, m.p. 171-178°, $[\alpha]^{30}\mathrm{D}$ $+14.85°$ (32% racemization).

C. **2-Hydroxy-1,1'-binaphthyl in *p*-Cymene.**—A solution of 1.0 g. of I, $[\alpha]\mathrm{D}$ $+21.70°$, in 30 ml. of *p*-cymene was heated at reflux for 3 days. The solution was cooled, extracted with three 30-ml. portions of 25% sodium hydroxide, the aqueous extracts chilled in ice and acidified with hydrochloric acid. The precipitate was filtered off, washed with water and dried. The crude product had m.p. 185–187°. The observed rotation, $\alpha = +0.002 \pm 0.005°$ (*c* 5 in methanol, *l* 4), indicated that it was optically inactive. Recrystallization from aqueous methanol gave needles, m.p. 188.5–189.5°, alone or mixed with (±)-I.

Reaction of 2-Hydroxy-1,1'-binaphthyl Phenylglyoxylate with Methylmagnesium Iodide. A. The Racemic Ester.—A solution of 10.0 g. of the racemic phenylglyoxylate in 150 ml. of dry ether was stirred and treated with 31 ml. of a *M* solution of methylmagnesium iodide in ether. The Grignard solution was added in ten equal portions at 3-minute intervals. After completion of the addition, the solution was heated at reflux for 30 minutes. Saturated ammonium chloride solution was added, the layers were separated, and the aqueous layer was extracted with three 75-ml. portions of fresh ether. The combined ether solutions were washed with water, sodium bicarbonate and water, dried over magnesium sulfate and evaporated. The resulting pale yellow oil was saponified with boiling 20% ethanolic potassium hydroxide for 4 hours. The reaction mixture was diluted with four times its volume of water and extracted with four 75-ml. portions of chloroform. The chloroform extracts were dried over magnesium sulfate and evaporated *in vacuo* to give 1.2 g. of a pale yellow oil (calculated as 1,1,2-trimethyl-2-phenylethylene glycol, 27%). The aqueous layer was acidified with hydrochloric acid and the precipitated solid was dissolved in ether and the aqueous solution was extracted with more ether. The combined ether extracts were extracted successively with three 50-ml. portions of 10% sodium bicarbonate and then with four 50-ml. portions of 25% sodium hydroxide. Evaporation of the ether left no residue. Acidification of the bicarbonate extract gave a precipitate. Extraction of the resulting mixture with ether, drying, and evaporation of the ether solution gave a crystalline residue, which, after being dried over concentrated sulfuric acid for 18 hours *in vacuo*, weighed 2.7 g. and had m.p. 87-89°, reported[18] for (±)-atrolactic acid, m.p. 93-94°. A mixture with an authentic sample of (±)-atrolactic acid of m.p. 93° melted at 92-93°. The sodium hydroxide extract was acidified with hydrochloric acid and the precipitate was filtered, washed with water and dried at 60° for 18 hours to give 6.3 g. of I, m.p. 185–187.5°.

B. **The (+)-Ester.**—The phenylglyoxylate of (+)-I, prepared from I of $[\alpha]\mathrm{D}$ $+21.70°$ in the same manner as the racemic phenylglyoxylate, had m.p. 154-156°, $[\alpha]^{30}\mathrm{D}$ $+32.50°$ in methanol when crude. Recrystallization from aqueous methanol and drying *in vacuo*, either at room temperature or at 60° for 48 hours, gave a hemihydrate, m.p. 156-157°, $[\alpha]^{30}\mathrm{D}$ $+32.64°$ (*c* 3.25 in methanol, *l* 4). The substance sublimed at 80° *in vacuo*. The infrared spectrum in chloroform was identical with that of the racemic phenylglyoxylate. The substance gave an immediate precipitate with 2,4-dinitrophenylhydrazine reagent.

Anal. Calcd. for $C_{28}H_{18}O_3 \cdot 0.5H_2O$: C, 81.74; H, 4.66. Found: C, 81.61, 81.50; H, 5.10, 5.00.

The Grignard reaction procedure was exactly the same as for the racemic ester with the exception that only the bicarbonate-soluble fraction was investigated. From 10.0 g. of (+)-phenylglyoxylate there was obtained 2.55 g. of atrolactic acid, m.p. 95–99°, $[\alpha]^{30}\mathrm{D}$ $-48.25°$ (*c* 7.05, *l* 4, in *M* sodium hydroxide[2c]). This corresponds to 85% optical purity.

Acknowledgment.—We are indebted to the National Science Foundation for financial support.

Los Angeles 7, California

---

[18] R. Fittig and C. Wurster, *Ann.*, **195**, 155 (1879).

[Contribution from the Department of Chemistry, Fordham University]

The Lead Tetraacetate Oxidation of *cis*- and *trans*-9,10-Diaryl-9,10-dihydro-9,10-phenanthrenediols. A Kinetic Study

By Emil J. Moriconi, Friedrich T. Wallenberger and William F. O'Connor

Received August 5, 1957

The rates of oxidation with lead tetraacetate in acetic acid are reported for a series of *cis*- and *trans*-9,10-diaryl-9,10-dihydro-9,10-phenanthrenediols in which the 9,10-diaryl substituents increase in bulk (aryl = 4-methylphenyl, 2,4-dimethylphenyl, 1-naphthyl, 2,4,6-trimethylphenyl, 2,3,5,6-tetramethylphenyl). There was no obvious correlation between rate data and intramolecular hydrogen bonding measurements. Reaction rates and calculated activation energies for both 9,10-dialkyl- and 9,10-diaryl-9,10-dihydrophenanthrenediols are interpreted within the framework of Criegee's cyclic intermediate or a cyclic transition state. The rate acceleration of the lead tetraacetate oxidations of *cis*- and *trans*-9,10-dihydro-9,10-phenanthrenediols and *cis*- and *trans*-9,10-di-(*p*-tolyl)-9,10-dihydrophenanthrenediols in relatively non-polar 99% benzene-1% acetic acid is also indicative of a cyclic process. Arguments against the Cordner–Pausacker mechanism are presented, and Criegee's recently suggested acyclic mechanism is discussed.

Criegee and co-workers[1-4] have extensively investigated the rate of cleavage of vicinal diols with lead tetraacetate. They have noted the pronounced difference in behavior of *cis*- and *trans*-isomeric diols and have enunciated the empirical rule that the *cis*-diols always show higher oxidation rates than do the isomeric *trans*-diols. Later work by Criegee,[5,6] Prelog,[7] and their co-workers has provided two general exceptions to the rule: (1) In unsubstituted, alicyclic diols, the $k_{\mathrm{cis}}/k_{\mathrm{trans}}$ ratio is greater than 1 only for those ring systems with seven or less carbon atoms. The ratio is re-

---

[1] R. Criegee, *Ber.*, **64**, 260 (1931).

[2] R. Criegee, L. Kraft and B. Rank, *Ann.*, **507**, 159 (1933).

[3] R. Criegee and E. Buchner, *Ber.*, **73**, 563 (1940).

[4] R. Criegee, E. Buchner and W. Walther, *ibid.*, **73**, 57 (1940).

[5] R. Criegee, B. Marchand and H. Wannowius, *Ann.*, **550**, 99 (1942).

[6] R. Criegee, E. Höger, H. Huber, P. Kruck, F. Marktscheffel and H. Schellenberger, *ibid.*, **599**, 81 (1956).

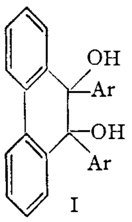
[7] V. Prelog, K. Schenker and H. H. Gunthard, *Helv. Chim. Acta*, **35**, 1598 (1952); V. Prelog, K. Schenker and W. Kung, *ibid.*, **36**, 471 (1953).

versed for rings composed of 9 or more carbon atoms. (2) In the 9,10-dihydro-9,10-phenanthrenediols and the 4,5-dihydro-4,5-pyrenediols, the k_{cis}/k_{trans} ratio is also less than 1 when the bridge carbon atoms contain either a hydrogen atom, methyl or ethyl group. This behavior is also noted in oxidations with *o*-nitrophenyliodosoacetate[3,8] or periodic acid.[3] Temperature and solvent apparently have no important influence on the ratio. With 9,10-aryl substituents, this ratio is reversed and the oxidation behavior then conforms to Criegee's rule.

Criegee[6] has rationalized this apparently anomalous behavior of unsubstituted alicyclic diols within the framework of his cyclic process[2,9] in which the *vic*-diols oxidize more rapidly the more the OH groups approach each other in a plane. Criegee[4] and Backer,[10] for example, have demonstrated that the rates of cleavage of racemic diols exceed those of *meso*-diols in the aliphatic series. Thus in the nine- or higher-membered rings of the alicyclic diols, conformational changes resulting from an increased flexibility of rings cause the *cis*-diols to attain the character of aliphatic *meso*-diols, and the *trans*-diols, that of the aliphatic *rac*-diols.[6]

In this paper we suggest that the behavior of diols in the dihydrophenanthrene series (and by analogy the dihydropyrene series)[11] also can be accommodated by Criegee's cyclic process or a cyclic transition state.

Recently we reported on the syntheses and intramolecular hydrogen bonding measurements of a series of *cis*- and *trans*-9,10-diaryl-9,10-dihydro-9,10-phenanthrenediols (I) in which the 9,10-diaryl substituents vary in bulk.[12]



I

Ia, Ar = 4-methylphenyl (*p*-tolyl)
Ib, Ar = 2,4-dimethylphenyl (*m*-xylyl)
Ic, Ar = 2,4,6-trimethylphenyl (mesityl)
Id, Ar = 2,3,5,6-tetramethylphenyl (duryl)
Ie, Ar = 1-naphthyl

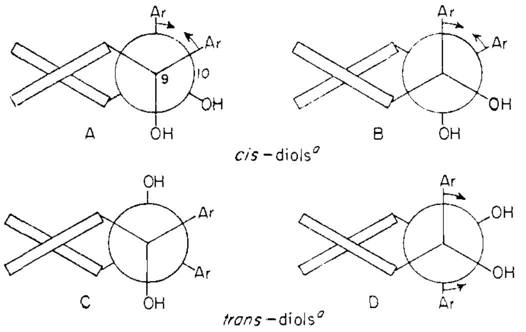
Intramolecular hydrogen bonding measurements in the *cis*-diol series showed hydrogen bonding between the *vic*-OH groups.[13] Of the *trans*-diols prepared, only the *trans*-di-(1-naphthyl)-diol (*trans*-Ie) showed any hydrogen bonding. Our data along with similar data for *cis*- and *trans*-9,10-dihydrophenanthrenediols (II), *cis*- and *trans*-9,10-dimethyl-9,10-dihydro-9,10-phenanthrenediols (IIIa) and *trans*-9,10-diisopropyl-9,10-dihydro-9,10-phenanthrenediol[14] (IV) are summarized in Table I.

TABLE I

FREQUENCY SHIFTS OF HYDROXYL BANDS IN THE INFRARED

	$\Delta\nu$(OH), cm.$^{-1}$ *cis*	*trans*
9,10-Dihydro-9,10-phenanthrenediol[15] (II)	38	0
9,10-Dimethyl-9,10-dihydro-9,10-phenanthrenediol[6] (IIIa)	27	0
9,10-Diisopropyl-9,10-dihydro-9,10-phenanthrenediol (IV)	..	0
9,10-Di-(*p*-tolyl)-9,10-dihydro-9,10-phenanthrenediol (Ia)	47	0
9,10-Di-(*m*-xylyl)-9,10-dihydro-9,10-phenanthrenediol (Ib)	56	0
9,10-Di-(1-naphthyl)-9,10-dihydro-9,10-phenanthrenediol (Ie)	63	36
9,10-Dimesityl-9,10-dihydro-9,10-phenanthrenediol (Ic)	69	..
9,10-Diduryl-9,10-dihydro-9,10-phenanthrendiol (Id)	65	..

We offered the following interpretation of the experimental results: in the *cis* series there is considerable steric interference between the two aryl groups and between the aryl groups and the biphenyl moiety, as can be seen in the two possible low energy skew conformations A and B. This steric interference can be relieved by increasing the Ar–C–C bond angles at positions 9 and 10 which at the same time decreases the O–C–C– bond angles, and consequently brings the equatorial OH bond and the axial OH bond closer together. In the *trans* series steric considerations would indicate D as the favored conformation. The infrared evidence, however, suggests conformation C for all the *trans*-diols reported herein, except *trans*-di-(1-naphthyl)-diol (*trans*-Ie). In *trans*-diol Ie, the very large naphthyl groups probably force it into conformation D.



cis-diols[a]

trans-diols[a]

[a] These convenient conformational symbols for the two-carbon bridged system in the *cis*- and *trans*-9,10-diaryl-9,10-dihydro-9,10-phenanthrenediols are adapted from those originally reported by Professor K. Mislow for a four-carbon bridge system in lectures presented at the AAAS Symposium on Organic Reaction Mechanisms, Dec., 1956, N. Y. Academy of Science, Jan., 1957; and N.Y. Am. Chem. Soc. Meeting-in-Miniature, Feb., 1957; and from Professor M. S. Newman's projectional formulas, *J. Chem. Ed.*, **32**, 344 (1955).

---

(8) J. P. Cordner and K. H. Pausacker, *J. Chem. Soc.*, 102 (1952); K. H. Pausacker, *ibid.*, 107 (1952).

(9) R. Criegee, *Sitzungsber. Ges. Naturwiss. Marburg*, **69**, 25 (1934); R. Criegee, *Ann.*, **522**, 75 (1936); *Angew. Chem.*, **50**, 153 (1937).

(10) H. J. Backer, *Rec. trav. chim.*, **57**, 967 (1938).

(11) The molecule of 9,10-dihydrophenanthrene can be regarded as having a collinear diphenyl skeleton with two benzene rings twisted at an angle of 20° (G. H. Beaven, D. M. Hall, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, 854 (1952). In the 4,5-dihydropyrene system, the planar phenanthrene frame must accommodate the two methylene groups in its 4,5-positions. Fisher–Taylor–Hirschfelder models indicate that substituents on the ethane bridge of both these compounds have approximately the same conformational relationship to each other.

(12) E. J. Moriconi, F. T. Wallenberger, L. P. Kuhn and W. F. O'Connor, *J. Org. Chem.*, **22**, 1651 (1957).

(13) The reported order of increasing, substituent bulk effect (Ia, Ib, Ie, Ic and Id) on *vic*-diol properties is based on hydrogen bonding measurements[12] and kinetic data reported herein on these diols, and infrared and ultraviolet absorption studies on the 2,2'-diaroylbiphenyls from which the *cis*-diols of this series were prepared.[12]

(14) This *trans*-diol was generously supplied by Prof. R. Criegee, Technische Hochschule, Karlsruhe, Germany. Its preparation is detailed in ref. 6.

TABLE II

RATES OF REACTION OF *vic*-DIOLS WITH LEAD TETRAACETATE IN 99.7-99.8% ACETIC ACID[a]

Compound	k_{20}			k_{30}			k_{40}		
	cis	*trans*	k_{cis}/k_{trans}	*cis*	*trans*	k_{cis}/k_{trans}	*cis*	*trans*	k_{cis}/k_{trans}
II	10.0[b]	157[b]	0.0637	29.3	460	0.0637	76.1	1270	0.0599
IIIa	7.50[c]	192[c]	0.0391	24.1[c]	507[c]	0.0475	.....	....	.....
IIIb	304[c]	1310[c]	0.232	....	....	.....	.....	....	.....
IV	.....	105[d]	......	....	248[d]	.....	.....	538[d]	.....
V	268[c]	24.7[c]	10.9	682[c]	69.3[c]	9.84	.....	....	.....
Ia	402	33.9	11.9	757	81.0	9.35	1390	189	7.35
Ib	139	11.2	12.4	215	19.2	11.2	303	28.6	10.6
Ie	81.1	9.80	8.28	154	20.1	7.66	292	34.7	8.41
Ic	7.28	.....	......	12.2	....	.....	17.0	....	.....
Id	0.568	.....	......	1.10	....	.....	1.97	....	.....

[a] All k-values are second-order rate constants in glacial acetic acid (mole^{-1} l. min.$^{-1}$). [b] Our work; Criegee[6] obtained k-values of 9.7 and 130, respectively, for *cis*-II and *trans*-II diols. [c] Criegee's data.[6] [d] Our work on Prof. R. Criegee's sample. Criegee[6] reports a k-value of 100.

In the present work, the rates of reaction of compounds Ia to Ie, *cis*- and *trans*-II and *trans*-IV with lead tetraacetate in 99.7–99.8% acetic acid have been measured at three different temperatures and are shown in Table II; data obtained by Criegee[6] for diols *cis*- and *trans*-IIIa, *cis*- and *trans*-9,10-diethyl-9,10-dihydro-9,10-phenanthrenediols (IIIb) and *cis*- and *trans*-9,10-diphenyl-9,10-dihydro-9,10-phenanthrenediols (V) are included for comparison. Table III summarizes activation energies (E) and frequency factor (A) calculated from rate data in Table II.

TABLE III

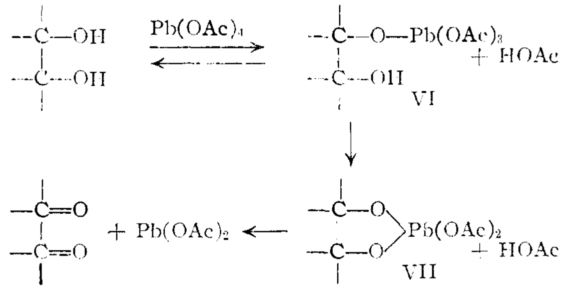
CALCULATED ACTIVATION ENERGIES (E) AND FREQUENCY FACTORS (A)

Compound	E, kcal./mole		A, mole^{-1} l. min.$^{-1}$	
	cis	*trans*	*cis*	*trans*
II	18.9	18.9	1.26×10^{10}	1.95×10^{16}
IIIa	20.5	17.1	1.52×10^{16}	1.50×10^{15}
IV	..	15.1	....	1.98×10^{13}
V	16.4	18.1	4.13×10^{14}	8.45×10^{14}
Ia	11.1	15.2	1.25×10^{11}	7.53×10^{12}
Ib	7.7	9.5	7.36×10^{7}	1.34×10^{8}
Ie	11.3	12.7	2.15×10^{10}	2.75×10^{10}
Ie	9.1	..	5.58×10^{7}	....
Id	11.6	..	5.01×10^{8}	....

Table II shows the k_{cis}/k_{trans} ratio for the 9,10-aryl substituted diols V and Ia-Ie, to be greater than 1, as anticipated. In the *cis*-diol series Ia-Ie there is observed an inverse relationship between intramolecular hydrogen bonding in the ground state and reaction rates.

Kuhn,[15,16] Prelog,[7] Criegee,[6] and Eliel[17] and coworkers have provided ample evidence that there is no simple correlation between reaction rates of *vic*-diol cleavage with lead tetraacetate and the strength of the hydrogen bond. One cannot conclude therefrom, however, that the distance between *vic*-OH groups is not the major factor that determines the reaction rate,[16] since such a comparison is based on a measurement made on a molecule at "rest" where conformational changes during chemical reactions are ruled out,[17] and a "reacting" molecule in an activated state. Criegee[6] has indicated that the energy requirements to reach the transition state would be much more relevant than rate data as an index of comparison between diols.

Reaction Mechanism.—Of the various mechanisms proposed for *vic*-diol cleavage with lead tetraacetate, most of the experimental evidence can be accounted for by Criegee's mechanism,[2,9] in which the rate-determining step is the formation of a five-membered cyclic intermediate VII.



However, although cyclic condensation products of *vic*-diols with ketones and with boric acid have been prepared, cyclic intermediate VII has never been isolated, nor, as Criegee himself has pointed out, is it adequate to explain the lead tetraacetate cleavage of *trans*-9,10-decalindiol[4] and *trans*-8,9-hydrindanediol.[18] Even a cyclic transition state seems incompatible with the relative conformation of OH groups in these compounds. The homolytic mechanism proposed by Waters[19] has been satisfactorily disproved by the work of Kharasch, Friedlander and Urry[20] who showed that acetoxy radicals furnished by acetyl peroxide do not cause diol fission. Similarly, the bimolecular fission suggested by Dewar[21] is not in accord with the evidence which excludes a free radical reaction with reasonable certainty.[6]

Alternatively, Cordner and Pausacker[8] have proposed a general cleavage mechanism applicable to all lead tetraacetate oxidations which involve a homolytic bond fission of the initially formed ester VI.

The most important feature of the Cordner–Pausacker theory is their explanation of the fact that

---

(15) L. P. Kuhn, THIS JOURNAL, **74**, 2492 (1952).

(16) L. P. Kuhn, *ibid.*, **76**, 4323 (1954).

(17) E. E. Eliel and C. Pillar, *ibid.*, **77**, 3600 (1955).

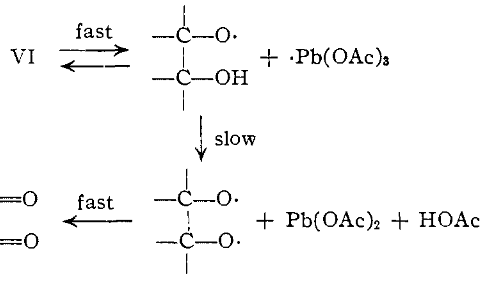
(18) R. Criegee and H. Zogel, *Ber.*, **84**, 215 (1951).

(19) W. A. Waters, "Chemistry of Free Radicals," Oxford Univ. Press, Oxford, Eng., 1946, p. 230.

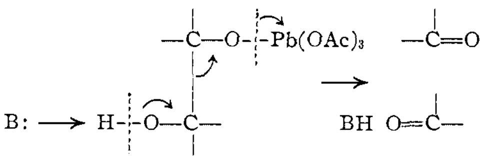
(20) M. S. Kharasch, H. N. Friedlander and W. H. Urry, *J. Org. Chem.*, **14**, 91 (1949).

(21) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford Univ. Press, Oxford, Eng., 1949, p. 276.

cis-diols react more readily than the *trans* compounds. They assume intramolecular hydrogen bonding for the *cis*-diols in which only one hydrogen participates in the hydrogen bonding, and intermolecular hydrogen bonding for the *trans*-diols in which both hydrogens participate with a consequent diminution in rate. We feel, however, that the strongest evidence against the Cordner–Pausacker mechanism is that under the concentrations in which the reaction rates are determined there is no evidence of intermolecular hydrogen bonding for the *trans*-diols, even in the ground state. Hydrogen bonding measurements[13,15,16] are made at diol concentrations of 0.005 *M* in carbon tetrachloride. Under these conditions, no measurable intermolecular hydrogen bonding has ever been found in *vic*-diols. In our kinetic studies, the concentration of reactants ranged from 0.0025 to 0.00125 *M* in acetic acid. Further, the presence in high concentrations of this strongly polar solvent is much more likely to lead to intermolecular acid–diol association, favored equally well by both *cis*- and *trans*-diols, than diol–diol association. Further, their reaction scheme does not explain: (a) the very large difference observed in the rates of *cis*-diol compared to *trans*-diol oxidations[22]; (b) the observed k_{cis}/k_{trans} ratio (less than one) for the unsubstituted (II), and alkyl substituted (IIIa, IIIb) 9,10-dihydro-9,10-phenanthrenediols; and (c) why this ratio is reversed (k_{cis}/k_{trans} ratio greater than one) when the hydrogen or alkyl substituent is replaced by an aryl group (V, Ia-Ie) in these diols.



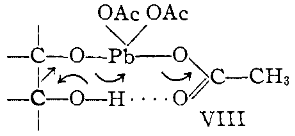
Criegee[6] has recently suggested an alternate, acyclic mechanism which avoids the assumption of cyclic intermediate VII. It has as its driving force the tendency of Pb(IV) to abstract an electron pair from the acetoxy-oxygen attached to it. In Criegee's formulation, the Lewis base (B:) affecting proton removal could be a solvent molecule of acetic acid, water or alcohol.



VI

Further, if the nucleophilic carbonyl oxygen atom of an acetate group already bonded to Pb acts as the Lewis base, the reaction would involve a concerted electron displacement *via* VIII.

Thus by assuming VI as an intermediate product, and depending on the proximity of the OH groups in the reacting molecule, the oxidation could proceed *via* cyclic intermediate VII or a cyclic transition state, or, as in the case of *trans*-9,10-decalindiol and *trans*-8,9-hydrindanediol, *via* acyclic paths, VIII, or reaction of VI with the solvent acting as a Lewis base.



VIII

It is pertinent that these two are the only diols reported whose reaction rate is retarded on solvent change from the polar glacial acetic acid to relatively non-polar 99% benzene–1% glacial acetic acid. Since this rate retardation may be indicative of an acyclic process,[23] we have oxidized *cis*- and *trans*-II diols ($k_{cis}/k_{trans} < 1$) and *cis*- and *trans*-Ia diols ($k_{cis}/k_{trans} > 1$) with lead tetraacetate in the 99% benzene–1% glacial acetic acid solvent. Results given in Table IV show an increase in reaction rate in all cases.

TABLE IV

RATES OF REACTION OF *vic*-DIOLS WITH LEAD TETRAACETATE IN 99% BENZENE-1% ACETIC ACID

Diol	k_{20} Acetic acid	k_{20} 99% Benzene–1% acetic acid	$k_{C_6H_6-AcOH}/k_{AcOH}$
cis-II	10.0	5,300	530
trans-II	157	>10,000	>63.7
cis-Ia	402	6,100	15.2
trans-Ia	33.9	605	17.8

In addition a comparison of activation energies suggests that both steric and polar factors may be responsible for the oxidative behavior of the *vic*-diols reported herein. This interpretation, like that suggested for the unsubstituted, alicyclic diols, is not inconsistent with cyclic intermediate VII or a cyclic transition state.

In general, to form VII or a cyclic transition state the *cis*-diols can react with lead tetraacetate as A or B, whereas the reacting molecule in the *trans*-diols must approach conformation D. Thus in the *trans*-diols series, any steric or electronic effect which would favor conformation D and hinder free rotation about the 9,10-carbon-carbon bond to C, as indicated by the arrows, should lower the activation energy for reaction.

cis- and *trans*-II show the same activation energies, despite the fact that the *trans*-II reacts approximately 16 times faster than the *cis*-II. Thus, at least when Ar = H, there must be no difference, energy-wise, between equilibrium interconversions A $\rightleftarrows$ B, and C $\rightleftarrows$ D.[24] This conclusion is in agree-

---

[22] H. M. Wasserman in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 386.

[23] We are grateful to Professor S. J. Angyal, New South Wales University of Technology, Australia for this suggestion.

[24] In the *cis*-9,10-dihydro-9,10-phenanthrenediols one OH group is equatorial and the other axial (A or B). In the *trans*-diols, both OH groups are axial (C) or equatorial (D). This conformational orientation is similar to that encountered in the most stable, chair form of *cis*- and *trans*-1,2-cyclohexanediols. In these alicyclic diols, the calculated distance between O-atoms for both *cis*- and *trans* compounds is 2.86 Å. (S. J. Angyal and C. G. MacDonald, *J. Chem. Soc.*, 686 (1952)). In *trans*-1,2-cyclohexanediol, equivalent to conformation C, the calculated distance between O-atoms is 3.66 Å. However, $\Delta\nu$(OH) meas-

ment with Howlett's[25] calculated 1.4 kcal./mole as the lowest energy pass above the ground state between antipodal equilibrium conformations in the simple 9,10-dihydrophenanthrene system. This low energy barrier is similar in magnitude to those separating rotational isomers which are not isolable as chemically distinct species.[26]

In *cis*-diols IIa and IIb, models indicate that the equatorial alkyl group overlaps both the equatorial OH group and a hydrogen atom attached to the biphenyl moiety.[27] In *trans*-diols IIa and IIb, both the bulk and the repulsive effect of the alkyl substituents probably force these reacting diols into conformations D. In this favored conformation, models also indicate some crowding of the two equatorial OH groups closer together both by the alkyl substituents and the hydrogens of the biphenyl moiety.

In the *cis*- and *trans*-diaryl substituted diols V and Ia-Ie, the lower activation energies in general may be attributed to the inductive effect of the aryl substituents on the 9,10-carbon atoms. An increased electron density at these positions would lead to their greater susceptibility to oxidation. In *trans*-diol V, models indicate that the planar phenyl substituent can adopt conformations which offer less steric interference to conformational equilibration $D \rightleftarrows C$ than do the alkyl substituted diols. This relative ease of interconversion and lack of a favored conformation could account for the $k_{cis}/k_{trans} > 1$.

Compound Ia differs from V only by a *p*-methyl substituent, yet *k*-values for both *cis*- and *trans*-Ia diols are correspondingly higher and activation energies lower than for the *cis*- and *trans*-V diols. In the benzpinacol series, Cordner and Pausacker[3] have also found that the presence of an electron-releasing substituent (CH_3, OCH_3) on the aryl group increases the reaction rate and lowers the activation energy. Theoretically in the oxidation process the formation of VI would be favored by an increased availability of electrons on the oxygen atom, thus displacing the equilibrium to the right.[8] As the reaction temperature is increased, this electronic effect decreases and the rates approach each other. The polar effect of *o*- and *p*-methyl substituents is also noticeable in the low activation energies of the *cis*- and *trans*-Ib diols. The slight increase in the activation energy from *cis*-Ib and *cis*-Ic may be attributed to increased steric interactions caused by the introduction of two additional methyl groups into an already "crowded" system. The buttressing effect of a *m*-methyl substituent in Id, clearly apparent in spectral data of similarly substituted compounds,[28–30] is indicated by a higher activation energy for Id as compared to Ic.

Experimental

Preparative details and physical properties of *cis*- and *trans*-diols Ia-Ie and II may be found in ref. 13. Method and apparatus for $\Delta\nu$(OH) measurements reported in Table I may be found in ref. 13, 15 and 16. Lead tetraacetate was obtained from Arapahoe Chemicals Inc., Boulder, Colo. The purity (92.5%) was determined by iodimetric titration with 0.002 *N* thiosulfate solution standardized against iodine in potassium iodide. Eastman Kodak Co. highest purity acetic acid, m.p. of 16.0–16.2° corresponding to a water content of 0.2–0.3% water,[8,31] was used as solvent for both diols and lead tetraacetate.

Kinetic Runs.—The kinetic runs were carried out in "Dreischenkelrohr"[32] tubes using Criegee's fast method. Previously determined solutions (1 ml. of each) of lead tetraacetate (0.005 *M*) and diol (0.005 *M*) in 99.7–99.8% acetic acid were placed in each of the lower bulbs of the "Dreischenkelrohr." Five ml. of "stopping solution" (20 g. of potassium iodide and 500 g. of sodium acetate in 1 l. of water) was placed in the side bulb. The solutions for the different runs were thermostated at 20.00, 30.00 and 40.00 ± 0.05° for 20 minutes to attain temperature equilibrium, after which the reaction solutions were mixed (concn. of lead tetraacetate and diol now 0.0025 *M*) and, at a definite time, the "stopping solution" was added. The iodine liberated was then back-titrated with 0.002 *N* thiosulfate solution.[33] Five to nine individual measurements were taken at each temperature.

Because of increasing insolubility, the *cis*- and *trans*-di-(1-naphthyl)-diols Ie and the *cis*-diduryldiol Id were run, respectively, in 0.0025 and 0.00125 *M* solutions in acetic acid before mixing. In each case, however, 2 ml. of each of the reactants was used. Table V summarizes typical variations of *k* for *cis*-diol Ib at 20°, *trans*-diol Ia at 30° and *cis*-diol Ie at 40°. The kinetics of diol cleavage are clearly second order, in agreement with all previous work in this field.

---

urements by Kuhn[15] and Eliel[17] show stronger hydrogen bonding for the *cis*- (39 cm.$^{-1}$) than the *trans*-1,2-cyclohexanediol (32 cm.$^{-1}$) in the ground state of these molecules, and the kinetic response of these diols to oxidation with lead tetraacetate in acetic acid shows a k_{cis}/k_{trans} ratio $\simeq$ 22.5 at 20°.[2,4] This behavior has been ascribed to the difference in energy required to bring the OH groups closer together by rotation about the C–C bond.[15] Such a deformation to bring the equatorial and axial OH groups closer together in the *cis*-diol decreases the pucker of the ring, whereas a deformation to bring the two equatorial OH groups together increases the pucker. Thus "for a given expenditure of energy, the OH groups of the *cis*-1,2-cyclohexanediol can get closer than the *trans*-1,2-cyclohexanediol."[15] Although this explanation may have some validity in the case of *cis*-9,10-dihydro-9,10-phenanthrenediols, this interpretation is probably not valid in the case of *trans* series since the twist incurred by the biphenyl moiety as the interplanar angle is increased would more likely lead to bond rupture at the 9,10-bridge.

If the reaction of *vic*-diols with lead tetraacetate is used as a test reaction for the relative position of OH groups,[17] then the rate data indicate that the OH groups in *trans*-diols II, IIa and IIb are closer than in the corresponding *cis*-diols. Models suggest to us a possible explanation for this proximity. In *cis*- and *trans*-1,2-cyclohexanediols, there seems to be no steric interference to free rotation of the OH groups by any of the axial or equatorial hydrogens. In *cis*-II there is some overlap of the equatorial OH group with a hydrogen of the biphenyl moiety. In *trans*-II, however, the van der Waals radii of both equatorial OH groups overlap hydrogens of the biphenyl moiety. This intramolecular "crowding" in *trans*-II, IIa and IIb could account for the observed k_{cis}/k_{trans} ratio <1.

(25) K. E. Howlett, *J. Chem. Soc.*, 125 (1955).

(26) K. S. Pitzer, THIS JOURNAL, **70**, 2140 (1948).

(27) The forty-fold increase in reaction rate from *cis*-IIIa to *cis*-IIIb can be attributed to the relative size of a CH_3 substituent as compared to a CH_2 group. When the substituents on the 9,10-carbons are primary alkyl groups, all but the CH_2 groups attached directly to these carbons can adopt conformations such that they cause little or no additional interference. The intensity of the steric effect observed on replacement of a CH_3 group by a C_2H_5, *n*-C_3H_7, etc., substituent depends on the sensitivity of the probe. Thus only second-order differences are noted in the ultraviolet absorption of mono-*o*-substituted biphenyls, and mono-*o*-substituted acetophenones—E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3154 (1955), and E. A. Braude and W. F. Forbes, *ibid.*, 3776 (1955). However, since electronic spectra are a less sensitive index of steric effects than reaction rates (E. A. Braude, F. Sondheimer and W. F. Forbes, *Nature*, **173**, 117 (1954); E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955)), the significant reaction rate increase is not unexpected.

(28) E. A. Braude and W. F. Forbes, *ibid.*, 3776 (1955).

(29) W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, **35**, 488 (1957).

(30) W. F. Forbes, F. T. Wallenberger, W. F. O'Connor and E. J. Moriconi, *J. Org. Chem.*, in press.

(31) Fr. Rudorff, *Ber.*, **3**, 390 (1870).

(32) R. Criegee, *Ann.*, **495**, 211 (1932).

(33) If a precipitate of lead iodide formed, it was not removed by filtration before titration.[8] This technique differs from that reported by R. P. Bell, J. G. R. Sturrock and R. L. St. D. Whitehead, *J. Chem. Soc.*, 82 (1940).

Activation energies (*E*) and frequency factors (*A*) were calculated from rate data using *k*-values at 20 and 30°. Although it would have been possible to extrapolate *E* and *A* from the individual Arrhenius plots consisting of three points at three different temperatures, this procedure was preferred so as to make our data comparable to that available from Criegee's work.

TABLE V

TYPICAL VARIATIONS OF *k*

Time, min.	$S_2O_3^=$, ml.	$a - x$	x	k
Compound *cis*-Ib; init. concn. of reagents 0.0025 *M* at 20° in 2.0 ml. of reacn. mixt.				
0.0	5.00	0.00250	0.00000	...
.4	4.38	.00219	.00031	141
.5	4.24	.00212	.00038	143
1.0	3.72	.00186	.00064	137
2.0	2.96	.00148	.00102	138
3.0	2.50	.00124	.00126	135
			Average	139
Compound *trans*-Ia; init. concn. of reagents 0.0025 *M* at 30° in 2.0 ml. of reacn. mixt.				
0.0	5.00	0.00250	0.00000	...
.2	4.80	.00240	.00010	83.3
.5	4.54	.00227	.00023	81.5
1.0	4.16	.00208	.00042	80.8
1.5	3.36	.00168	.00082	78.1
3.0	3.12	.00156	.00094	80.3
4.0	2.74	.00137	.00113	82.5
			Average	81.0
Compound *cis*-Ie; init. concn. of reagents 0.00125 *M* at 40° in 4.0 ml. of reacn. mixt.				
0.0	5.00	0.001250	0.000000	...
.1	4.66	.001165	.000085	299
.2	4.38	.001095	.000155	285
.3	4.12	.001030	.000220	287
.4	3.88	.000970	.000280	293
.5	3.70	.000925	.000325	294
			Average	292

Acknowledgment.—We are indebted to Professor R. C. Fuson, University of Illinois, and Professor R. Criegee, Technische Hochschule, Karlsruhe, Germany, for furnishing some of the diols used in this work. We wish to thank Dr. L. P. Kuhn, Aberdeen Proving Grounds, Aberdeen, Md., for the infrared measurements and Dr. D. J. Hennessy, Fordham University, for many helpful discussions. We also take pleasure in thanking the Research Corporation and the National Science Foundation for grants supporting this work.

NEW YORK 58, N. Y.

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

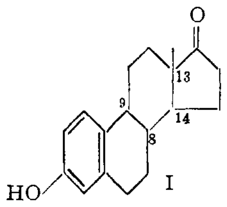
Configuration of the Estrones. Total Synthesis of the Remaining Stereoisomers

BY WILLIAM S. JOHNSON, ISRAEL A. DAVID,[1] HENRY C. DEHM,[2] ROBERT J. HIGHET,[3] E. W. WARNHOFF,[4] W. DAVID WOOD[5] AND E. T. JONES[6]

RECEIVED JULY 24, 1957

Seven of the eight possible racemic forms having the estrone structure have now been synthesized in our laboratory. Five of these, α-1, α-2, β-1, β-2 (*dl*-estrone), and 14-isoestrone, were obtained in former studies and two, γ-1 and γ-2, are described in the present work. Experiments and arguments are presented for the assignments of configurations to each of these products as represented in Chart 4. The interrelationships among our isomers and those of other workers has been considered (see Table II). It has been demonstrated that Anner and Miescher's isomers a, d and f probably correspond to our substances 14-iso-, α-2 and γ-1 estrone, respectively. In addition it appears likely that Bachmann's estrone isomer is identical with estrones f and γ-1. By a process of elimination Anner and Miescher's isomer e accounts for the eighth racemate. A stereochemical rationale is presented for the method by which the isomers of Anner and Miescher and of Bachmann were produced. Independent evidence is presented which establishes the B/C *trans* configuration of estrone in the classical manner through relationship to substances of unequivocal configuration.

The estrone structure (I) contains four dissimilar asymmetric carbon atoms (C_8, C_9, C_{13} and C_{14}); hence there are 16 optical isomers or 8 *dl*-forms theoretically possible. The configurations for one of the enantiomers of each of these 8 *dl*- pairs are depicted in Chart 4.



I

A number of racemic products corresponding to the estrone structure already have been prepared.[7-10] Five different *dl*-forms of estrone, α-1, α-2, β-1, β-2 (natural), and 14-iso, have been produced previously in our own laboratory.[9,10] The present work discloses (a) the synthesis of two additional racemates, γ-1 and γ-2; (b) evidence

---

(1) Allied Chemical and Dye Corp. (National Aniline Division) Fellow, 1953–1954.

(2) Research Assistant supported by G. D. Searle and Co., 1953; and E. I. du Pont de Nemours and Co., summers 1950–1953.

(3) Research Assistant supported by the Wisconsin Alumni Research Foundation, 1950–1951; Allied Chemical and Dye Corp. Fellow, 1952–1953.

(4) Socony-Vacuum Co. Fellow, 1951–1952; Homer Adkins Fellow, 1952–1953.

(5) Research Assistant supported by grants from the Wisconsin Alumni Research Foundation, The National Science Foundation and G. D. Searle and Co., 1954–1956; and E. I. du Pont de Nemours and Co., summer, 1953.

(6) National Science Foundation Predoctoral Fellow, 1956–1957.

(7) W. E. Bachmann, S. Kushner and A. C. Stevenson, THIS JOURNAL, **64**, 974 (1942).

(8) (a) G. Anner and K. Miescher, *Helv. Chim. Acta*, **31**, 2173 (1948); (b) **32**, 1957 (1949).

(9) W. S. Johnson, D. K. Banerjee, W. P. Schneider, C. D. Gutsche, W. E. Shelberg and L. J. Chinn, THIS JOURNAL, **74**, 2832 (1952).

(10) (a) W. S. Johnson, R. G. Christiansen and R. E. Ireland, *ibid.*, **79**, 1995 (1957); (b) W. S. Johnson and W. F. Johns, *ibid.*, **79**, 2005 (1957).