heating a solution of the diol in a 50% aqueous acetic acid solution (containing 5% sulfuric acid) for 20 min on a steam bath, mp 71–72°. Two recrystallizations from methanol–water followed by two recrystallizations from hexane did not change the melting point. The nmr spectrum in chloroform or carbon tetrachloride showed only three peaks. The vinyl protons appeared as a triplet at $\delta = 5.53$ ppm; the $-CH_2O$ group protons appeared as a singlet at $\delta = 4.14$ ppm while the allylic and $-CH_3$ protons appeared together as a sharp singlet at $\delta = 2.04$ ppm; infrared spectrum, 1735 cm^{-1}. *Anal.* Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 68.95; H, 7.93. The acetate was also prepared from acetic anhydride and pyridine but the product was harder to purify.

The residue from the ethyl acetate crystallization of the diol was chromatographed on 140 g of silicic acid in a 3.7 × 27 cm column; 100-ml fractions were collected. Fractions 14–22, eluted with 5% ethyl acetate in benzene, contained the pure acyloin V, 0.96 g (10.1%). Fractions 23–24, 0.13 g, contained a mixture of the acyloin and the hemiacetal IV. Fractions 25–38 were pure hemiacetal, 0.61 g (6.4%). The solvent mixture was changed slowly from 5 to 20% ethyl acetate and fractions 76–87 gave an additional 0.55 g of diol for a total of 2.03 g (21.1%). Nothing else could be eluted.

The hemiacetal showed infrared bands in chloroform at 3600 and 3380 cm^{-1} for –OH. The region between 2800 and 1670 cm^{-1} was virtually transparent. A very weak band, 6% below the base line, appeared at 1720 cm^{-1} for the aldehyde which is likely to be present in equilibrium with the hemiacetal. The nmr spectrum gave no evidence, however, for any significant quantity of aldehyde. In chloroform the vinyl protons appeared as a poorly resolved multiplet at $\delta = 5.56$ ppm; the single methinyl hydrogen adjacent to –O– and –OH appeared as a partially resolved doublet at $\delta = 5.30$ ppm; the –OH proton is also a poorly resolved doublet at $\delta = 4.6–4.95$ ppm; the protons of the $-CH_2O-$ appear as an AB quartet at $\delta = 3.90$ and 3.55 ppm, $J = 7.6$ cps; the allylic protons appear as a group of multiplets from $\delta = 2.67$ to 1.40 ppm with the principal peak at $\delta = 2.08$ ppm. In deuteriochloroform the spectrum is very similar except that the –OH peak overlaps the downfield doublet of the AB group at 35° and the upfield doublet at 60°. The peak positions are shifted *ca.* 1 or 2 cps. The lone methinyl hydrogen appears as a doublet at $\delta = 5.3$ ppm, $J = 6$ cps. In dimethyl sulfoxide the –OH proton moves downfield to $\delta = 6.23$ ppm and the methinyl hydrogen slightly upfield to $\delta = 5.17$ ppm. Both are well resolved doublets, $J = 5.5$ cps.[16] Five recrystallizations from 5:1 hexane–benzene gave the analytical sample, mp 97.0–98.0°. *Anal.* Calcd for $C_{16}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.09; H, 8.29.

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[16] *Cf.* O. L. Chapman and R. W. King, *J. Am. Chem. Soc.*, **86**, 1256 (1964).

The Chromic Acid Oxidation of Diastereoisomeric 1,2-Diols[1]

Ned D. Heindel, Edward S. Hanrahan,
and Richard J. Sinkovitz

*Department of Chemistry, Marshall University,
Huntington, West Virginia*

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In chromic acid oxidations of *cis*- and *trans*-1,2-dimethyl-1,2-cyclopentanediol, Rocek and Westheimer reported a *cis/trans* rate ratio of 800 in 90% acetic acid[2] compared to a *cis/trans* ratio of 320 reported by Criegee for lead tetraacetate cleavages in the same system.[3] Since stereochemical principles[4] and hydrogen-bonding studies[5] point to the fact that the diastereoisomeric symmetrical dialkyldiarylethanediols would be excellent acyclic models for the more rigid *cis–trans* systems and, since Criegee has already reported a *dl/meso* rate ratio of 2.9/1 for lead tetraacetate oxidation of 2,3-diphenyl-2,3-butanediol,[3] we proposed to investigate the chromic acid cleavages in this system.

Considerable evidence is available in the literature supporting a five-membered cyclic chromate ester intermediate in the oxidative scission of 1,2-diols.[2,6,7] Repeated comparisons have been made with the well-known lead tetraacetate cleavage of pinacols and glycols in which a cyclic plumbate ester has been postulated to justify the considerably faster rates obtained with *cis*-diols.[3]

Pure diastereoisomeric forms of 2,3-diphenyl-2,3-butanediol (I) and 4,5-diphenyl-4,5-octanediol (II) were synthesized according to published procedures[5] and were oxidized as 5.0×10^{-3} and 10.0×10^{-3} *M* solutions in 55% dioxane–45% water containing 0.10 *M* perchloric acid, 0.30 *M* sodium perchlorate, and 5×10^{-4} to 10.0×10^{-4} *M* chromic acid (as CrO_3).

Because of the exceedingly fast reaction velocities observed with I in acetic acid–water reaction medium it was necessary to modify conditions to obtain a measurable rate. With a solvent of lower dielectric, dioxane–water, and a spectral method to follow chromium(VI) loss at 3500 A, it was possible to obtain convenient and reproducible rate data in the 15–25° range. No temperature conditions were available at which the isomers of I could be directly compared in relative rate to the isomers of II. Since the latter compounds oxidized with great reluctance at ambient temperatures, they were studied at 40°. The 2,3-diphenyl-2,3-butanediols demonstrated immeasurably rapid rates at 40° and these were studied at 20°. See Table I for kinetic data.

Table I[a]

Compound	Temp, °C	Diol, *M*	*k*,[b] min^{-1}
I mixed			
isomers[c]	25	0.005	0.83
isomers[c]	25	0.01	2.06
isomers[c]	25	0.01	2.00[d]
meso	20	0.01	1.28
meso	20	0.01	1.35[d]
dl	20	0.01	1.46
dl	20	0.01	1.48[d]
II *meso*	40	0.005	0.045
dl	40	0.005	0.088

[a] All runs performed at 0.10 *M* perchloric acid, 0.30 *M* sodium perchlorate, and 5×10^{-4} *M* chromic acid. [b] The *k*'s are pseudo-first-order rate constants. [c] Because of the difficulty in obtaining pure forms of the diastereoisomers, initial oxidations were performed on mixtures to establish reaction conditions. [d] Occasional runs were calculated by the classical graphic method to verify conformity with the Swinbourne computer technique.

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[1] (a) Supported in part by Petroleum Research Fund Grant 222-G to N. D. H. and by Marshall University Research Board Benedum Faculty Fellowships to N. D. H. and E. S. H. (b) Taken in part from the M.S. Thesis of R. J. S., Marshall University, 1965. (c) Presented at the Southeast–Southwest Regional Meeting of the American Chemical Society, Memphis, Tenn., Dec 3, 1965.

[2] J. Rocek and F. H. Westheimer, *J. Am. Chem. Soc.*, **84**, 2241 (1962).

[3] R. Criegee, E. Hoger, G. Huber, P. Kruck, F. Marktscheffel, and H. Schellenberger, *Ann.*, **599**, 81 (1956).

[4] L. Kuhn, *J. Am. Chem. Soc.*, **80**, 5950 (1958); E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., New York, N. Y., 1962, p 138.

[5] W. A. Mosher and N. D. Heindel, *J. Org. Chem.*, **28**, 2154 (1963).

[6] H. Kwart, J. A. Ford, Jr., and G. C. Corey, *J. Am. Chem. Soc.*, **84**, 1252 (1962).

[7] Y. W. Chang and F. H. Westheimer, *ibid.*, **82**, 1401 (1960).

Both I and II demonstrated pseudo-first-order behavior with respect to chromium disappearance. Previous workers have reported that the reaction displays over-all third-order kinetics, first order in acid, chromium(VI), and diol.[2,7]

The only previous studies on the oxidation of *dl*- and *meso*-pinacol isomers were reported by Bretzger[8] who observed a 1.3/1 relative ratio for the rates of 3,4-diphenyl-3,4-hexanediols (*dl*/*meso*) at 30° in 90% acetic acid with no added mineral acid.

Similarly, we have found only a small rate difference in the diastereoisomers of I and the diastereoisomers of II. The *dl*/*meso* ratio of 2,3-diphenyl-2,3-butanediol (I) was found to be 1.1/1 at 20°, and in4,5-diphenyl-4,5-octanediol (II) a 1.9/1 ratio was observed at 40°. Regrettably no experimental conditions could be found to provide comparison at identical temperatures.

The mere existence of an accelerated rate for the *dl* isomers, whose sterically favored conformer possesses nearly *cis* hydroxyls, compared with the *meso* isomer where skew hydroxyl alignment would generate severe aryl–aryl interactions, is not sufficient information to justify the cyclic diester. Indeed the small rate differences could more properly be explained if the reaction were assumed to involve a noncyclic monoester of chromic acid oxidizing through a hydrogen-bonded system linking the chromate to the adjacent hydroxyl.

In oxidative cleavages in 1,2-dimethyl-1,2-cyclopentanediol the origin of the *cis* faster than *trans* rate effect has been ascribed to the allowed formation of the cyclic diester for the *cis* and the necessitating assumption that a different noncyclic transition state must attain for *trans*.[2] With the diastereoisomeric diols included in this study, a cyclic diester would be possible for both *dl* and *meso* forms, although it would be expected that if the rate step were the decomposition of such a diester, the *meso* isomer ought to show a steric acceleration. Such an acceleration is unobserved.

Furthermore, it would be expected that the diphenyloctanediols (II) should show considerably faster oxidation rates than the diphenylbutanediols (I) since a significant increase in steric strain, in the cyclic diester, should accompany the lengthening of the chain from methyl to *n*-propyl. Hydrogen-bonding studies have demonstrated that appreciable Thorpe–Ingold compression of the O–C–C bond angle exists in the octanediols (II) ($\Delta\nu = 50$ cm^{-1}) compared with the butanediols (I) ($\Delta\nu = 35$ cm^{-1}).[5] This bond-angle deformation ought to accelerate further the oxidations of II with respect to I if a diester cycle were undergoing rate-determining decomposition.

Actually the diphenyloctanediols are at least 20 times slower than the diphenylbutanediols (see Table I), a difference which would almost certainly be greater if they could be experimentally compared at the same temperature.

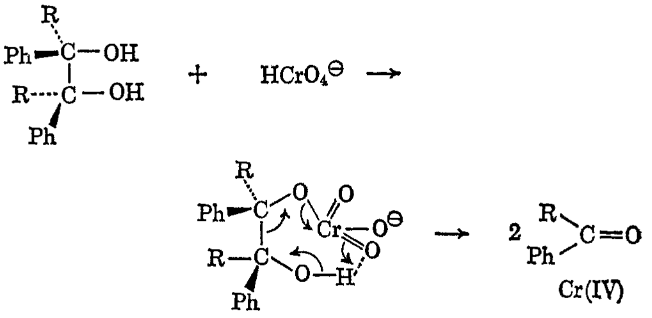
This suggests that perhaps in these acyclic diols the rate-determining process is the formation of the chromate ester and that ester decomposition is a relatively rapid phenomenona. Although it has been claimed that chromate esterifications are relatively insensitive to steric effects[6] there do exist definite precedents for rate-determining esterifications. The 18β-12-oleanene shows rate-determining character in the formation of its chromate ester.[9]

Kwart and Bretzger have employed rate-determining esterification to explain the cleavage rate differences in cyclohexanone and cyclopentanone diols.[10]

Attempts to prepare cyclic acetonide derivatives of the diols I and II have been unsuccessful in our hands, an additional reflection of the steric hindrance to attack at the carbinol sites.

The steric hindrance to esterification can be cited as the cause of the major rate differences between I and II, but in order to account for the small observed variations in the *dl vs. meso* isomers it is necessary to assume that the two adjacent hydroxyls must in some way participate in forming the reactive intermediate of the rate process. We suggest that the data can best be rationalized by assuming a monoesterification leading to a seven-membered hydrogen-bonded structure in the slow step of the reaction.

Developing interactions of the adjacent skewed groups in formation of the cycle would be somewhat greater for the *meso* than for the *dl* isomers, and an explanation for the small differences in reaction velocity would be provided.



Similar hydrogen-bonded intramolecular hydrogen-abstracting intermediates have been proposed for the oxidations of alcohols.[11]

Experimental Section

Preparation of Starting Materials.—All diols employed in this study were prepared by published procedures detailed in ref 5 and were demonstrated to be pure by comparison with the published spectral bands and melting points.

Dioxane was carefully purified by the method of Fieser.[12]

Kinetic Measurements.—The rate of disappearance of chromic acid was measured by the change in absorbance of the reaction solutions at 250 mμ in a Beckman Model DB spectrophotometer. Solutions 0.100 *M* in diol in dioxane were thermostated at the reaction temperature. An aliquot of diol solution was transferred to a thermostated flask containing sodium perchlorate, perchloric acid, chromic acid, water, and dioxane in sufficient amounts to bring the final concentrations of all components to the desired values. The reactants were mixed by rapidly swirling the flask, and a portion of the resulting solution was transferred to a Pyrex cell in the thermostated cell cavity of the spectrophotometer. Absorbance readings were taken at definite time intervals from the spectrophotometer dial and a continuous plot of per cent transmittance *vs.* time was also obtained using a constant-speed recorder attached to the spectrophotometer. Infinite time absorbances were obtained after 24 hr.

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[8] D. Bretzger, Ph.D. Thesis, University of Delaware, 1964.

[9] J. Rocek, F. H. Westheimer, A. Eschenmoser, L. Moldovanyi, and J. Schreiber, *Helv. Chim. Acta*, **45**, 2554 (1962).

[10] H. Kwart and D. Bretzger, *Tetrahedron Letters*, **No. 45**, 3985 (1965).

[11] H. Kwart, *Suomen Kemistilehti*, **A34**, 173 (1961).

[12] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1957, pp 284, 285.

Pseudo-first-order rate behavior was checked by the differential method.[13]

Kinetic Analysis of Data.—Conventional techniques for determining rate constants for first-order reactions require a measurement of the reaction variable at "infinite time," *i.e.*, after several half-lives. This infinite time reading is then used in the calculation of all data points so that the accuracy of the result depends almost entirely on the accuracy of this single measurement.

Swinbourne[14] has shown that this objection can be readily overcome. In order to take advantage of this little used but elegant method, a computer program was developed for the IBM 1620 which carries out a least-squares analysis of the data obtained in accordance with the Swinbourne method. Results were checked by comparison with conventional techniques using the infinite time technique.

Reactant Stability and Product Identification.—Solutions of the diols in the reaction medium lacking the oxidant were found to be stable throughout the reaction lifetime, ruling out the possibility of appreciable pinacol rearrangement.

The only products obtained from the oxidation were the expected acetophenone from I and *n*-butyrophenone from II, identified as their 2,4-dinitrophenylhydrazones by comparison with authentic samples.

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[13] K. J. Laidler, "Chemical Kinetics," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1965, p 15.

[14] E. S. Swinbourne, *J. Chem. Soc.*, 2371 (1960).

Stereochemistry of Diels–Alder Adducts of Bi-1-cyclohexen-1-yl

RICHARD K. HILL AND HUGH J. BARGER, JR.[1]

Frick Chemical Laboratory, Princeton University,
Princeton, New Jersey

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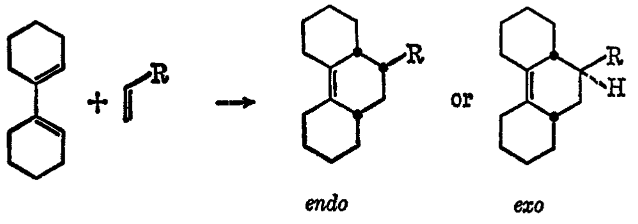
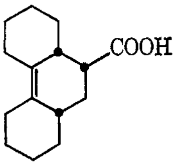
The most direct synthetic route to simple derivatives of the hydrophenanthrene skeleton involves Diels–Alder addition of dienophiles to bi-1-cyclohexen-1-yl.[2] When the dienophile is a monosubstituted olefin, two stereoisomeric adducts are possible, one resulting from *endo* orientation of the addends and one from *exo* addition.

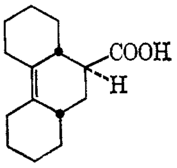


Many of the reported additions do lead to a mixture of both isomeric adducts, whereas in other cases apparently only one isomer is formed. Alder's rule[3] of "maximum overlap of unsaturation" leads to the prediction that the *endo* isomer should predominate, although the possibility that steric interference in the transition state might favor *exo* addition[4] cannot be ruled out.

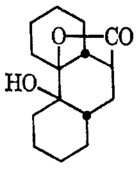
When this investigation was begun, no evidence was available for the configuration of any adducts of bi-1-cyclohexen-1-yl. Recently Christol and Levy[5] offered arguments favoring the *endo* configuration for the acrylic acid adduct (I). Diels–Alder addition furnishes a single product, mp 185°, although the epimeric acid (II), mp 130°, may be obtained by alkaline isomerization of I and its derivatives. The French workers oxidized both acids with osmium tetroxide; adduct I gave a nonlactonizable dihydroxy-acid, while II afforded, in addition to an isomeric dihydroxy acid, a 5% yield of the hydroxy lactone III. On the assumption that osmium tetroxide attacks exclusively from the less hindered side of the double bond, the 185° adduct was assigned the all-*cis* configuration I.



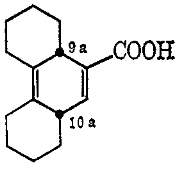
I



II



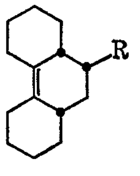
III



IV

To provide independent confirmation for this assignment, we have now been able to prepare acid I by partial hydrogenation of the propiolic acid adduct IV. At 5000 psi, over platinum at room temperature (conditions chosen to favor rapid, stereospecific reduction[6]), IV was hydrogenated cleanly to the acrylic acid adduct I. Since hydrogenation under these conditions should result in addition of hydrogen from the less hindered side of the double bond, in this case *cis* to the hydrogens at 9a and 10a, the product may be assigned the all-*cis* configuration.

Adducts in which the 9-substituent is cyano, formyl, carbomethoxy, carboxamido, and acetyl have all been related to the acrylic acid adduct I.[2,5] We have extended these stereochemical correlations to the nitroethylene adduct V. Reduction of V and acetylation gave amide VI. The same amide was produced by Beckmann rearrangement of the oxime (VII) of the methyl vinyl ketone adduct, as well as by acetylation of the amine formed by Curtius rearrangement of I. Addition of nitroethylene to bi-1-cyclohexen-1-yl is thus another Diels–Alder reaction which gives exclusively *endo* addition.



V, $R = NO_2$
VI, $R = NHCOCH_3$
VII, $R = C(CH_3) = NOH$

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[1] Acknowledgment is gratefully made to the American Machine and Foundry Co. and to the Proctor and Gamble Co. for fellowships to H. J. Barger, Jr.

[2] E. Bergmann, H. Davies, and R. Pappo, *J. Org. Chem.*, **17**, 1331 (1952).

[3] K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

[4] For exceptions to the rule of *endo* addition, see J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

[5] H. Christol and M. Levy, *Bull. Soc. Chim. France*, 3056 (1964).

[6] R. L. Burwell, Jr., *Chem. Rev.*, **57**, 895 (1957).