Compound Ie (195 mg.), dissolved in ethanol and treated with a slight excess of 2,4-dinitrophenylhydrazine in phosphoric acid,[44] gave 400 mg. (90%) of the **2,4-dinitrophenylhydrazone**, m.p. 170–171° after recrystallization from ethanol; ultraviolet spectrum: λ_{max}^{MeOH} 361 mμ, log ε 4.37; 352 mμ (shoulder), log ε 4.16; 229 mμ, log ε 4.24.

Anal. Calcd. for $C_{16}H_{16}N_4O_4$: C, 58.5; H, 4.9; N, 17.1. Found: C, 58.3; H, 4.7; N, 17.0.

Ketone Ie (538 mg.) in ethanol in the presence of 5% Pd-on-C (113 mg.) absorbed 3.0 moles of hydrogen in 65 minutes. Evaporation of the solvent and distillation afforded **cycloheptylacetone** (**IId**) as a colorless liquid, b.p. 54–55° (0.5 mm.), $n^{25}D$ 1.4629; infrared spectrum (liquid, 0.025-mm. cell): peaks at 2930, 1715, 1465 and 1454 (doublet), 1405, 1352, 1270, 1235, 1183, 1155 and 953 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.9; H, 11.8. Found: C, 78.7; H, 11.9.

The 2,4-dinitrophenylhydrazone of IId was obtained in 93% yield, m.p. 125–126° after recrystallization from aqueous ethanol; ultraviolet spectrum: λ_{max}^{MeOH} 362 mμ, log ε 4.49; 264 mμ (shoulder), log ε 4.14; 230 mμ, log ε 4.34.

Anal. Calcd. for $C_{16}H_{22}N_4O_4$: C, 57.5; H, 6.6; N, 16.8. Found: C, 57.9; H, 6.9; N, 16.7.

Compound Ie was also obtained by distillation of the forerun from the preparation of Ib. The pale yellow liquid had a b.p. of 52–55° (0.1 mm.), but its infrared spectrum showed bands (particularly at 818, 797 and 780 cm.$^{-1}$) not present in the spectrum of pure Ie. A sulfur-containing impurity was found to be present, arising from the quinoline used in the preparation of Ib. The 2,4-dinitrophenylhydrazone prepared from the impure ketone was identical with that described above.

Maleic Anhydride Adducts IIIa-d.—With the exception of IIIa, these were prepared by refluxing equimolar amounts of triene and maleic anhydride in dry benzene for 24 hours.[18]

(a) **Compound IIIa from Cycloheptatriene.**—This compound was prepared as described by Kohler, *et al.*[45] Three recrystallizations from hexane gave colorless needles, m.p. 103–104° (reported 102–104°,[39] 104–105°[19]). The infrared spectrum (KBr) shows strong bands at 3025, 2960, 1870 and 1840 (doublet), 1800, 1237, 1105, 1090, 1004, 972, 958 and 953 (doublet), 929, 918 (shoulder), 853, 833, 741, 743 and 739 (doublet) cm.$^{-1}$.

(b) **Compound IIIb from Phenylcycloheptatriene.**—The adduct was isolated by the addition of pentane. The crystals, m.p. 128–133° (42%), were recrystallized twice from benzene–pentane to furnish colorless needles, m.p. 136–137° (reported[18] for the adduct of Ib from biphenyl and diazomethane, 131–132°); infrared spectrum (KBr): prominent peaks at 3040, 2960, 1830, 1760, 1480, 1430, 1225, 1087 and 1070 (doublet), 1037, 997, 958 and 948 (doublet), 921, 858, 841, 822, 761, 718, 702 and 692 (doublet) cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.7; H, 5.3; mol. wt., 266. Found: C, 76.6; H, 5.3; mol. wt., 278.

(c) **Compound IIIc from *p*-Chlorophenylcycloheptatriene.**—The turbid solution resulting from the addition of pentane to the cooled reaction mixture deposited crystals, m.p. 120–125° (22%), on standing in the cold for several weeks. Three recrystallizations from benzene–pentane gave colorless prisms, m.p. 129–130°; infrared spectrum (KBr): prominent bands at 3000, 1855, 1775, 1485, 1225 (shoulder), 1215, 1095, 1073, 1010 and 1003 (doublet), 947, 922 (shoulder), 918 and 903 (doublet), 862, 848, 830 and 822 (doublet,) 803 and 737 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{13}ClO_3$: C, 67.9; H, 4.4; Cl, 11.8. Found: C, 68.1; H, 4.1; Cl, 11.7.

From the attempted hydrogenation, at atmospheric pressure, of IIIb in ethyl acetate in the presence of PtO_2 only unchanged starting material, identified by mixture m.p. and infrared spectrum, could be isolated.

(d) **Compound IIId from *p*-Nitrophenylcycloheptatriene.**—The reaction mixture began to deposit crystals after a few hours of heating. Filtration gave the adduct in 98% yield, m.p. 238–239°. The colorless prisms obtained by three recrystallizations from ethyl acetate had the same melting point; infrared spectrum (KBr): prominent bands at 3050, 2940, 1850, 1770, 1595, 1520, 1340, 1223, 1105, 1081, 1061, 989, 920, 887, 863, 841, 821, 803 and 747 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{13}NO_5$: C, 65.6; H, 4.2; N, 4.5. Found: C, 65.3; H, 4.3; N, 4.7.

New York 53, N. Y.

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(44) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., D. C. Heath and Co., Boston, Mass., 1955, p. 316.

(45) E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, This Journal, **61**, 1057 (1939).

[Contribution from the Department of Chemistry, Fordham University, New York, 58, N. Y.]

Oxidation Kinetics of *vic*-Diols in Cyclic Systems. II.[1a] Lead Tetraacetate Oxidation of *cis*- and *trans*-1,2-Diaryl-1,2-acenaphthenediols[1b]

By Emil J. Moriconi, William F. O'Connor, Elizabeth A. Keneally and
Frederick T. Wallenberger

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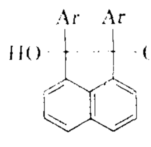
The rates of oxidation with lead tetraacetate in acetic acid are reported for a series of *cis*- and *trans*-1,2-diaryl-1,2-acenaphthenediols which varied in bulk and electronic effects [aryl = phenyl (Ia), 4-methylphenyl (Ib), 2,4-dimethylphenyl (Ic), 2,4,6-trimethylphenyl (Id) and α-naphthyl (Ie)]. *cis*-I (H), *cis*-II (methyl), *cis*-Ia and *cis*-Ie diols, and all the *trans*-diols showed true second-order kinetics. *cis*-Ib and *cis*-Ic diols at 20°, and *cis*-Ie diol at 40° simultaneously underwent a partial pinacol rearrangement. Rate retardation was observed in the lead tetraacetate oxidations of *trans*-Ia, *trans*-Ib and *trans*-Ic diols in relatively non-polar 99% benzene–1% acetic acid and is suggestive of an acyclic mechanism. All other diols can be mechanistically accommodated by Criegee's cyclic intermediate or cyclic transition state. There was no correlation between reaction rates and intramolecular hydrogen bond strengths.

Recently[2] we reported on the synthesis and intramolecular hydrogen bonding measurements of a series of *cis*- and *trans*-1,2-acenaphthenediols in which the 1,2-aryl substituents varied in bulk and electronic effects.



I, Ar = H
Ia, Ar = phenyl
Ib, Ar = 4-methylphenyl (*p*-tolyl)
Ic, Ar = 2,4-dimethylphenyl (*m*-xylyl}
Id, Ar = 2,4,6-trimethylphenyl (mesityl)
Ie, Ar = α-naphthyl

Both *cis*- and *trans*-diols displayed high frequency bands (3584–3600 cm.$^{-1}$) which were as-

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(1) (a) Part 1, E. J. Moriconi, F. T. Wallenberger and W. F. O'Connor, This Journal, **80**, 656 (1958); (b) Presented in part at the Meeting-in-Miniature, Metropolitan Long Island Subsection, American Chemical Society, New York Section, March, 1958, and at The 134th Meeting of The American Chemical Society, Chicago, Ill., September, 1958.

(2) E. J. Moriconi, W. F. O'Connor, L. P. Kuhn, E. A. Keneally and F. T. Wallenberger, This Journal, **81**, 6472 (1959).

TABLE I

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

Compound	k_{20}		k_{30}		k_{40}	
	cis	*trans*	*cis*	*trans*	*cis*	*trans*
I	120,000[4,5]	0.03[4,5]	.....	...	..	.....
II	28,600[4,5]	0.06[4,5]	60,600[4,5]	...	..	.....
Ia	33,000[b]	282[b]	53,100[d]	684[d]	..	1600
Ib	.....[c]	689	.....[c]	1640	..[c]	3970
Ic	.....[c]	369	.....[c]	834	..[c]	1820
Id	.....	1.34	.....	4.08	..	6.90
Ie	11,500	424	28,800	926	..[c]	2010

[a] All *k*-values are second-order rate constants in glacial acetic acid (l. mole^{-1} min.$^{-1}$). [b] Our work; Criegee[4,5] obtained *k*-values of 33,100 and 284, respectively, for *cis*-Ia and *trans*-Ia diols. [c] Diols partially rearranged in solvent acetic acid to form pinacol product; data in Table III; see discussion and experimental; [d] Our work; Criegee[4,5] obtained *k*-values of 53,000 and 682, respectively, for *cis*-Ia and *trans*-Ia diols.

TABLE II

CALCULATED ACTIVATION ENERGIES, FREQUENCY FACTORS, AND ENTHALPIES AND ENTROPIES OF ACTIVATION

Compound	*E*,[a] kcal./mole		*A*,[a] mole^{-1} l. min.$^{-1}$		ΔH^*,[b] kcal./mole		ΔS^*,[b] e.u.	
	cis	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
II	13.2	..	2.17×10^{14}	....	12.6	..	−38.1	....
Ia	8.4	15.6	5.99×10^{10}	1.29×10^{14}	7.8	15.0	−37.8	−47.2
Ib	..	15.3	....	1.78×10^{14}	..	14.7	....	−45.5
Ic	..	14.4	....	1.98×10^{13}	..	13.8	....	−46.7
Id	..	19.6	....	6.01×10^{14}	..	19.0	....	−57.9
Ie	16.2	13.7	1.38×10^{16}	6.55×10^{12}	15.6	13.1	−39.9	−46.4

[a] Calculated using Arrhenius equation ($k = Ae^{-E/RT}$) from rate data at 20 and 30°. [b] Calculated using Eyring's equation ($k = (\mathbf{k}T/H)\, e^{\Delta S^*/R}\, e^{-\Delta H^*/RT}$).

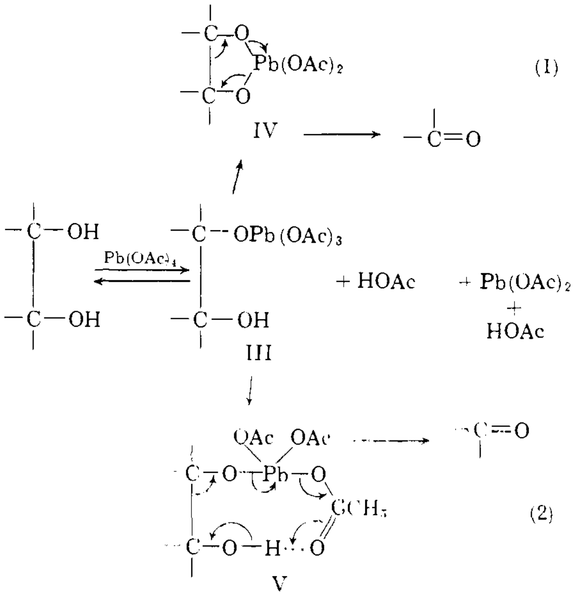
signed to a weak OH$\cdots\pi$ bond to the naphthalene ring of the acenaphthene system. The lower frequency bands (3512–3542 cm.$^{-1}$) in the *cis*-diols and the 3544 cm.$^{-1}$ band in *trans*-Ie diol were assigned to a stronger OH$\cdots$O bond between *vic*-diols, while the intermediate frequency bands (3549–3574 cm.$^{-1}$) in the aryl substituted *trans*-diols were uniquely assigned to an OH$\cdots\pi$ electron bond to the aromatic ring of the aryl substituent situated on the adjacent carbon atom. In none of the diols was a really "free" OH absorption (>3620 cm.$^{-1}$)[3] observed.

In the present work, the rates of oxidation of compounds Ia to Ie with lead tetraacetate in 99.7–99.8% acetic acid have been measured at 20°, 30° and 40°, and are shown in Table I; data obtained by Criegee[4,5] for *cis*- and *trans*-1,2-acenaphthenediols (I) and *cis*- and *trans*-1,2-dimethyl-1,2-acenaphthenediols (II) are also included. Table II summarizes activation energies (*E*), frequency factors (*A*) and thermodynamic functions of activation calculated from rate data in Table I.

Experimental

All diols were prepared as described in a previous paper.[2] The reaction rate was studied by previously outlined methods.[1a,6] Diol concentrations were approximately 0.005 *M* in 99.7–99.8% acetic acid or in 99% benzene-1% acetic acid with the single exception of *trans*-Ic diol which was approximately 0.003 *M* in acetic acid. The lead tetraacetate concentration for the oxidation of *trans*-Ic diol was 0.00165 *M* in acetic acid; for all other diols, 0.00274–0.00279 *M* in acetic acid. All runs with diols which showed second-order rate constants were reproducible to within 3%. Data for those diols which showed anomalous behavior are summarized in Table III.

Reaction Mechanism.—There is common assent to the view that no single mechanism prevails in the oxidation of *vic*-diols with lead tetraacetate. The two most generally accepted mechanisms have been proposed by Criegee.[4,5,7,8] Both involve the initial, reversible formation of a covalent O–Pb bond (III), followed by a rate-determining step whose driving force is the electronegativity of Pb(IV) which abstracts the bonded electron pair of one of the O-atoms adjacent to the C–C bond. The most favorable reaction path 1, requires the formation of a five-membered cyclic intermediate IV.[4,5,7] For those diols, such as *trans*-9,10-decalindiol[9,18] and *trans*-8,9-hydrindanediol[10] which are incapable of forming ring structures but nevertheless undergo oxidative cleavage by lead tetraacetate, alternative mechanisms include: a concerted electron displacement (electrophilic–nucleophilic) within a cyclic transition state (V)[8] *via* pathway 2, Brönsted base-catalysis *via* sequence 3,[8] or acid-catalysis *via* sequence 4.[11] Pathway 2



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[3] As for example in *cis*- and *trans*-1,2-cyclopentanediols, respectively, 3633 and 3620 cm.$^{-1}$ [L. P. Kuhn, THIS JOURNAL, **74**, 2492 (1952)].

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

[5] R. Criegee, *Sitzber. Ges. Beforder. ges. Naturw. Marburg*, **69**, 25 (1934).

[6] R. Criegee, *Ann.*, **495**, 211 (1932).

[7] R. Criegee, *ibid.*, **522**, 75 (1936); *Angew. Chem.*, **50**, 153 (1937).

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

[9] R. Crieger, E. Büchner and W. Walther, *Ber.*, **73**, 571 (1940).

[10] R. Criegee and H. Zogel, *ibid.*, **84**, 215 (1951).

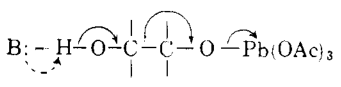
[11] R. P. Bell, V. G. Rivlin and W. A. Waters, *J. Chem. Soc.*, 1696 (1958).

Table III

Diol	Concentration, mM.	Temp., °C.	Time, min.	0.002 N $S_2O_3^=$, ml.	Oxidation, %	Pinacol rearrangement, %
cis-1b	2.78	20.00 ± 0.05	0.00	5.50	0.0	0.0
			.10	5.82		
			.20	5.54		
			.30	5.42		
			1.00	5.42	92.4	7.6
		30.00 ± .05	0.00	5.50	0.0	0.0
			0.75	3.23		
			1.00	3.22		
			1.50	3.22	41.5	58.5
		40.00 ± .05	0.00	5.50	0.0	0.0
			1.00	3.23		
			1.50	3.23		
			11 hr.	3.22	41.5	58.5
cis-1c	2.78	20.00 ± .05	0.00	5.50	0.0	0.0
			0.80	4.84		
			2.00	4.92		
			6.00	4.92	10.6[a]	89.4[a]

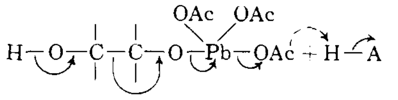
[a] At 30° and 40°, a similar ratio of rearrangement and oxidation was observed.

is a specific example of the general ionic theory of oxidations of organic compounds in acidic solution proposed by Levitt.[12]



(3)

III



(4)

The weight of evidence against[1a,8,13,14] the alternative Cordner–Pausacker mechanism[15] has led Pausacker to abandon it in favor of a Criegee-type mechanism[16] with the restriction promulgated by Hughes–Ingold[17] that any intramolecular change proceeding through a cyclic transition state is never exclusively electrophilic, nucleophilic or homolytic in character but is a hybrid of all three processes.

In conformity with Criegee's rule,[4,5,9,18] the *cis*-1,2-acenaphthenediols reported herein were oxidized more rapidly with lead tetraacetate, and with *o*-nitrophenyliodoso acetate[19] than the corresponding isomeric *trans*-diols whether the 1,2-bridge-carbon-atoms contain hydrogen (I), methyl (II) or aryl substituents (Ia–Ie). The oxidation of these diols, however, differs in this respect from the lead tetraacetate oxidation of 4,5-dihydro-4,5-pyrenediols,[8] and from the lead tetraacetate[1a,8] and *o*-nitrophenyliodoso acetate[20] oxidation of 9,10-dihydro-9,10-phenanthrenediols where Criegee's rule was followed only with aryl substituted compounds. In addition, oxidation rates of the acenaphthenediols are 100–1000 times faster than those of similarly substituted dihydrophenanthrene- and dihydropyrenediols. We ascribe these higher reaction rates to three factors: (i) The eclipsed conformation of substituents in the acenaphthenediols as compared to the skewed conformation of similar substituents in the dihydrophenanthrene- and diphydroyrenediols.[1a] (ii) The unusually long aliphatic C–C bond distance (1.644 Å.),[21] and the aliphatic bond angle (101°)[21] indicate a considerably strained ethane bridge.[22] Cleavage of this bond within the five-membered ring would convert these considerably strained tetrahedral C-atoms with a coördination number of 4 to normal carbonyl C-atoms with a coördination number of 3.[23] Consequently relief of angular strain at the acenaphthene bridge C-atoms (101° → 120°) would be greater than the corresponding deformation for tetrahedral C-atoms (109.5° → 120°).[24] (iii) The equatorial H-atoms immediately adjacent to the *vic*-diols in the 1,2-acenaphthenediols offer less steric interference to frontal attack by lead tetraacetate than similarly situated H-atoms in 9,10-dihydro-9,10-phenanthrenediols and 4,5-dihydro-4,5-pyrenediols. Thus there is presumably less F-strain in the reaction between acenaphthenediols and lead tetraacetate.

The order of reactivity within the series of *cis*- and *trans*-Ia to Ie diols in general seems to be sensitive to both steric and polar effects. In both series, negative $\Delta S^{\ddagger}$ values suggest that the formation of intermediate IV or transition state V is accompanied by an appreciable loss of entropy. The $\Delta S^{\ddagger}$ values for *trans*-diols Ia, Ib, Ic and Ie (except Id) are scattered around an average value of −46.5 e.u. (−45.5 to 47.2 e.u.). The same is true for *cis*-diols II, Ia and Ie (−37.8 to −39.9 e.u.; av., −38.6 e.u.). Thus transition states for both series of reactions are more rigid than the reactants, the highly ordered structures being more pronounced in the *trans*-diols than in the *cis*-diols.

In the *trans*-diols, increasing rate constants in the sequence, *trans*-Ia < *trans*-Ib can be rationalized in terms of the increasing electron-releasing powers of the substituents (in the sequence $C_6H_5 <$ *p*-$CH_3C_6H_4$) to the oxygen atom in the equilibrium formation of III. Combined and compensating steric and electronic factors place *trans*-Ie between *trans*-Ia and *trans*-Ib diols as far as rate constants are concerned. In *trans*-Ic and *trans*-Id diols, the rate constants reflect the increased steric interactions caused by the introduction of one or two additional methyl groups as *o*-substituents. *trans*-Id diol is of especial interest because of its extreme $\Delta S^{\ddagger}$ value and extraordinarily low rate constant. Conformationally it resembles all other diols in the *trans* series: the two hydroxyl groups are at the

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[12] L. S. Levitt, *J. Org. Chem.*, **20**, 1297 (1955).

[13] L. P. Kuhn, This Journal, **76**, 4323 (1954).

[14] D. H. Hey, C. J. M. Stirling and G. H. Williams, *J. Chem. Soc.*, 2747 (1954).

[15] J. P. Cordner and K. H. Pausacker, *ibid.*, 102 (1953).

[16] L. K. Dyall and K. H. Pausacker, *ibid.*, 3950 (1958).

[17] E. D. Hughes and C. K. Ingold, *Quart. Rev.* (*London*), **6**, 34 (1952).

[18] R. Criegee, *Ber.*, **64**, 260 (1931); R. Criegee and E. Büchner, *ibid.*, **73**, 563 (1940).

[19] E. J. Moriconi, W. F. O'Connor, E. A. Keneally and F. T. Wallenberger, unpublished results.

[20] E. J. Moriconi, C. K. Donovan, F. T. Wallenberger and W. F. O'Connor, Meeting-in-Miniature, Metropolitan Long Island Subsection, American Chemical Society, New York Section, March, 1958.

[21] A. I. Kitaĭgorodskiĭ, *Zhur. Fiz. Khim.*, **23**, 1036 (1949); *C. A.*, **44**, 897 (1950).

[22] A. G. Anderson, Jr., and R. G. Anderson, *J. Org. Chem.*, **22**, 1197 (1957).

[23] H. C. Brown and K. Ichikawa, *Tetrahedron*, **1**, 221 (1957).

[24] In this comparison it is tacitly assumed that the methylene bridge C-atoms in 9,10-dihydro-9,10-phenanthrenediols and in 4,5-dihydro-4,5-pyrenediols possess regular C–C bond distances and normal tetrahedral bond angles, as in cyclohexane.

bottom of a trough, on both sides of which are the two aryl substituents.[2] In such a model, a change in substituents from *m*-xylyl (Ic) to mesityl (Id) should certainly increase steric hindrance to reaction (the major contributing factor being the rigidity of the transition state) and the oxidation rate should therefore correspondingly decrease.

In the *cis*-diols, the decrease in rate from *cis*-I to *cis*-II diols can be attributed to the steric effect of the eclipsed methyl groups on the ease of formation of IV or V.[25] The most striking fact in the *cis*-diol series is the apparent competition between *vic*-diol oxidation and *pinacol rearrangement*. *cis*-Diols Ia and Ie, in agreement with general *vic*-diol oxidation kinetics, yield true second-order rate constants at 20 and 30°; *cis*-Ie showed visible sign of rearrangement at 40°. *cis*-Ib diol, differing from *cis*-Ia diol only by a *p*-methyl substituent, no longer followed second-order kinetics but apparently rearranged partially at 20° to form pinacol product (Table III). Similarly, *cis*-Ic and *cis*-Id diols showed no second-order kinetics, even at room temperature, The kinetics could not be run at lower temperatures because solvent acetic acid freezes at 16.0–16.2°. These observations are in agreement with the early investigations of the catalytic effect of acids, notably sulfuric, *p*-toluenesulfonic and trichloroacetic acid on the pinacol rearrangement of *cis*- and *trans*-Ia diols.[26,27] Indeed, Criegee and Plate[26] cautioned that boiling *cis*-Ia in solvent acetic acid rearranged this diol irreversibly into 2,2-diphenyl-1-acenaphthenone. Even in cold acetic acid on standing a few days, they observed a distinct decrease in diol content.

The activating effect of a *p*-methyl substituent on the migratory aptitude of symmetrically arylated pinacols in the pinacol rearrangement is fairly well substantiated within a given series of diols,[28] and nicely explains why *cis*-Ib undergoes partial rearrangement while *cis*-Ia shows second-order kinetics of *vic*-diol cleavage. The further addition of an *o*-methyl group on the aryl substituent in *cis*-Ic diol should enhance the migratory aptitude of the 2,4-dimethylphenyl substituent (Ic) relative to the 4-methylphenyl substituent (Ib),[29] since the bulkier substituents presumably would facilitate the removal of the adjacent hydroxyl group to form the carbonium ion for rearrangement. Thus *cis*-Ic diol is even less apt to undergo oxidative cleavage with lead tetraacetate than *cis*-Ib diol. The experimental results support this thesis.

Although it was not yet possible to separate the first-order rate constants of the rearrangement from the second-order rate constants of the oxidation, it was possible to estimate the approximate extent of rearrangement from the volume of unused thiosulfate titer. Thus at 20°, some 92.4% of *cis*-Ib diol was oxidized within 18 sec., the remaining 7.6% was simultaneously converted to rearrangement product; at 30 and 40°, some 41.5% of this same diol was oxidized and 58.5% simultaneously rearranged. *cis*-Ic diol rearranged to a much greater extent even at 20°: 89.4% rearrangement and only 10.6% oxidation, with approximately the same ratio of rearrangement and oxidation at 30° and 40°. In all these cases, an immediate, visible color change to yellow occurred on dissolution of the diol in solvent acetic acid.[30] No such color change was observed with those diols which yielded clearly and reproducibly second-order rate constants.

There remains to be explained why the lead tetraacetate oxidation of the *cis*-diols is accomplished by increasing amounts of pinacol rearrangements as one proceeds from Ia to Id, while in the same series, no such rearrangement is observed in the *trans*-diols. Bartlett and Brown[27] have established that *cis*-Ia is transformed smoothly into 2,2-diphenyl-1-acenaphthenone when treated with sulfuric or *p*-toluenesulfonic acid. However, *trans*-Ia reacted sluggishly and the rearrangement to identical 2,2-diphenyl-1-acenaphthenone is apparently preceded by isomerization of *trans*-Ia to *cis*-Ia. Confirmation of this was obtained by these authors by isolation of *cis*-Ia diol from the rearrangement of *trans*-Ia diol which had proceeded only to the extent of 28%. It appears, therefore, that in this series only the *cis*- and not the *trans*-diol form can undergo the pinacol rearrangement.

As in previous studies[1a,8,13,31,32] a comparison of the data in Table I with $\Delta\nu$(OH) values[2] showed no correlation between reaction rates and intramolecular hydrogen bond strengths.

Criegee has noted that *trans*-9,10-decalindiol, *trans*-8,9-hydrindanediol and *trans*-Ia were the only diols to date whose *reaction rates were retarded* on solvent change from the highly polar glacial acetic acid to the relatively non-polar 99% benzene–1% glacial acetic acid. All other diols subjected to the same solvent change showed large rate enhancements.[1a,8] Models show that *trans*-9,10-decalindiol and *trans*-8,9-hydrindanediol cannot be oxidized *via* mechanisms which require either a cyclic intermediate IV, or cyclic transition state V, and it is therefore highly probable that these diols, even in acetic acid as solvent, must be oxidized *via* different mechanisms, such as in 3 or 4. If this implication holds true for all diols

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(25) V. G. Bulgrin and G. Dahlgren, Jr., THIS JOURNAL, **80**, 3883 (1958), report a similar rate decrease in the periodate oxidation of *cis*-1,2-cyclopentanediol and *cis*-1,2-dimethyl-1,2-cyclopentanediol. These authors also suggest that the two methyl groups may offer steric hindrance to formation of the postulated, rate-determining cyclic intermediate.

(26) R. Criegee and K. H. Plate, *Ber.*, **72**, 178 (1939).

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

(28) W. E. Bachmann and F. H. Moser, *ibid.*, **54**, 1124 (1932); W. E. Bachmann and J. W. Ferguson, *ibid.*, **56**, 2081 (1934).

(29) Although *ortho* substitution normally lowers the migratory aptitude of phenyl substituents in symmetrical pinacol systems,[28] it remained to R. F. Brown [THIS JOURNAL, **76**, 1279 (1954)] to show that *o*-substituted phenyls appeared to migrate as rapidly as *p*-substituted phenyls in the sulfuric–acetic acid-catalyzed rearrangement of *cis*- and *trans*-1,2-di-*o*-tolyl- and *cis*- and *trans*-1,2-di-*p*-tolyl-1,2-acenaphthenediols.

(30) As was also observed in the pinacol rearrangement of *cis*- and *trans*-9,10-dihydro-9,10-phenanthrenediols in acetic–sulfuric acid [E. J. Moriconi, F. T. Wallenberger, L. P. Kuhn and W. F. O'Connor, *J. Org. Chem.*, **22**, 1651 (1957); E. J. Moriconi, F. T. Wallenberger and W. F. O'Connor, *ibid.*, **24**, 86 (1959)].

(31) E. L. Eliel and C. Pillar, THIS JOURNAL, **77**, 3600 (1955).

(32) 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).

TABLE IV

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

Diol	k_{20} HOAc	k_{20} 99% C_6H_6–1% HOAc	$k_{C_6H_6-HOAc}/k_{HOAc}$
trans-I	0.03	30.0	1000
trans-II	0.06[a]	2.6[a]	43[a]
trans-Ia	282	151	0.54[b]
trans-Ib	689	348	.51
trans-Ic	369	339	.92
cis-Ic	...	80,300	...

[a] Criegee's data.[8] [b] Criegee obtained a ratio of 0.75.[8]

whose rates are retarded in solvent benzene, then important mechanistic conclusions can be derived from the data in Table IV. We have oxidized *trans*-I, *trans*-Ia, *trans*-Ib *and cis*- and *trans*-Ic diols with lead tetraacetate in the 99% benzene–1% acetic acid and found that all aryl substituted *trans*-diols showed a rate retardation. A rate increase was found for *trans*-I as with *trans*-II diols,[8] while a measurable rate was obtained for the first time for *cis*-Ic diol.[33] Thus the results strongly suggest mechanism 1 or 2 for *cis*- and *trans*-I and II diols as with most other diols,[1a,8] and some *alternative* mechanism, perhaps 3 or 4, for all the *trans*-1,2-diaryl-1,2-acenaphthenediols reported herein.

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[33] In this case, the concentration of acetic acid was probably too low to cause a measurable pinacol rearrangement.

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Dicarboxylation of Terphenyl

BY TOD W. CAMPBELL

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The Friedel–Crafts reaction of terphenyl with oxalyl chloride gives a high yield of 4,4''-dicarboxyterphenyl. A number of derivatives of this acid has been prepared, including a high molecular weight polyamide. The position of substitution has been shown unequivocally by conversion in four steps to the known 4,4''-dimethylterphenyl.

The synthesis of functionally substituted *p*-terphenyls is seldom straightforward and usually includes a coupling of aromatic systems, or formation of a ring by, for example, a Diels-Alder condensation. The field has been reviewed recently.[1] Direct substitution of *p*-terphenyl has yielded only a few derivatives. Thus, dinitration gives a mixture[2,3] while dibromination,[3-5] disulfonation[6] and diacylation[7,8] appear to take place in the 4- and 4''-positions. However, there is room for doubt regarding the position of substitution,[7,8] since reference compounds are lacking and the position of substitution has been assumed, not proved.

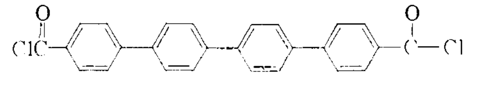
The carboxylation with oxalyl chloride[9] of terphenyl has now been investigated. and found to be a high-yield route to the previously unknown terphenyl-4,4''-dicarboxylic acid (I), the structure of which has been proved conclusively.

The dicarboxylation was carried out in carbon disulfide with excess oxalyl chloride and aluminum chloride in a yield of better than 90% of the acid after hydrolysis of the reaction mixture. The diacid formed pale yellow, high-melting leaflets. Interestingly, it was completely insoluble in aqueous potassium, sodium, lithium and ammonium hydroxides.

The diacid chloride II was readily prepared, as a pale yellow crystalline solid, soluble in many common solvents, easily hydrolyzed to the free diacid. It was readily converted to the dimethyl ester III. It was converted to a high molecular weight soluble polyamide (IV) by a low-temperature polymerization[10,11] with 2,5-dimethylpiperazine.

The structure of I and its derivatives was shown as follows. The acid chloride II was reduced with lithium aluminum hydride to the diol V, which was converted to the dihalide VI with thionyl chloride. Bis-(chloromethyl)-terphenyl was then hydrogenolyzed with lithium aluminum hydride to 4,4''-dimethylterphenyl (VII), identical to a sample prepared by an unequivocal route[12] (Fig. 1).

Attempts to dicarboxylate quaterphenyl and quinquephenyl[12] were not completely successful, although a small amount of crude quaterphenyldiacid chloride, probably the 4,4'''-derivative VIII,



VIII

was isolated. It was noteworthy for the very intense blue fluorescence of a dilute benzene solution even in diffuse sunlight.

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