

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF NOTRE DAME]

The Conformation of a Six-membered Ring *cis*-1,2 Fused to a Five-membered Ring<sup>1</sup>BY ERNEST L. ELIEL AND CONRAD PILLAR<sup>2</sup>

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The normally greater stability of *cis*-hydrindane systems as compared with the corresponding *trans*-hydrindanes has been explained by assuming either that the six-membered ring is in the boat form or that it is a slightly deformed chair, the deformation being more readily achieved for *cis*-fusion. That the latter explanation is the correct one has now been shown by a study of the rate of oxidation of the 2-oxa-*cis*-hydrindane-5,6-diols with lead tetraacetate. The ratio of the rate of cleavage of the *cis*-diol to that of the *trans*-diol is quite similar to the corresponding ratio for cyclohexane *cis*- and *trans*-1,2-diols and entirely different from that for cyclopentane *cis*- and *trans*-1,2-diols. The former two glycols are in the chair form while the geometry of the latter simulates the steric situation at the side of a boat. The conclusion that the six-membered ring in the *cis*-hydrindane system is in the chair form is supported by a study of the infrared absorption frequencies of the 2-oxa-*cis*-hydrindane-diols in the 2-3 $\mu$  region. The separation between the bands due to bonded and unbonded hydroxyl, in dilute solution, resembles that of the cyclohexanediols-1,2 and differs from that of the cyclopentanediols-1,2.

In most systems where a five-membered ring is fused to a six-membered ring and the relative stability of the *cis* and *trans* isomers has been determined by equilibration, the *cis* isomer has proved to be the more stable one.<sup>3-5</sup> Some notable exceptions are the parent compound hydrindane,<sup>6</sup> the corresponding 2-ketone (hydrindanone-2),<sup>7</sup> some 15-ketosteroids,<sup>8</sup> dimethyl- $\alpha$ -retrodendrin and isodesoxy-podophyllotoxin.<sup>9</sup> In the former two cases the order of stability is based on heat of combustion data,<sup>10</sup> in the latter cases on the failure of the *trans*-isomer to undergo epimerization.<sup>11</sup>

(1) Presented before the Organic Section at the National Meeting, Am. Chem. Soc., New York, N. Y., Sept. 15, 1954.

(2) This paper is taken in part from the Ph.D. dissertation of the Rev. Conrad Pillar, O.S.B.

(3) The evidence has been reviewed by (a) W. Hückel, "Theoretische Grundlagen der Organischen Chemie," Akademische Verlagsgesellschaft m.b.H., Leipzig, 1931, Vol. I, pp. 56-70; (b) R. P. Linstead, *Ann. Repts.*, **32**, 306 (1935); (c) R. B. Turner in L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Third Ed., Reinhold Publishing Corp., New York, N. Y., 1949, pp. 624-629; (d) W. E. Bachmann, A. Ross, A. S. Dreiding and P. A. S. Smith, *J. Org. Chem.*, **19**, 222 (1954); (e) A. S. Dreiding, *Chem. and Ind.*, 992 (1954). (In this last reference, the possibility that the six-membered ring might be a deformed chair—*cf.* ref. 15—appears to have been overlooked.)

(4) See also A. von Baeyer, *Ann.*, **258**, 217 (1890); W. Hückel and L. Schnitzspan, *ibid.*, **505**, 274 (1933); W. Hückel and E. Goth, *Ber.*, **67**, 2104 (1934); A. H. Cook and R. P. Linstead, *J. Chem. Soc.*, 956 (1934); C. K. Chuang, Y. L. Tien and Y. T. Huang, *Ber.*, **68**, 864 (1935); R. P. Linstead and A. F. Millidge, *J. Chem. Soc.*, 478 (1936); W. E. Bachmann and F. Ramirez, *THIS JOURNAL*, **72**, 2527 (1950); W. E. Bachmann and A. S. Dreiding, *ibid.*, **72**, 1323 (1950).

(5) W. Hückel, M. Sachs, J. Yantschulewitsch and F. Nerdel, *Ann.*, **518**, 155 (1935).

(6) G. Becker and W. A. Roth, quoted in ref. 5.

(7) W. A. Roth and F. Müller, quoted in ref. 3a and in ref. 12b.

(8) C. S. Barnes, D. H. R. Barton and G. F. Laws, *Chem. and Ind.*, 616 (1953).

(9) A. W. Schrecker and J. L. Hartwell, *THIS JOURNAL*, **75**, 5916 (1953); M. E. Cisney, W. L. Schilling, W. M. Hearon and D. W. Goheen, *ibid.*, **76**, 5083 (1954).

(10) The facts for *cis*- and *trans*-hydrindane have been confirmed by F. D. Rossini and C. C. Browne (private communication from Prof. F. D. Rossini) and will be discussed in detail by these authors.

(11) In 15-ketocholestanol, the side-chain at C<sub>17</sub> is *cis* to the angular methyl group at C<sub>13</sub>. Since the five-membered ring in *cis*-hydrindane is nearly planar (see discussion in this paper) while in *trans*-hydrindane it is quite puckered, there would be more eclipsing, and therefore more steric interference between the C<sub>13</sub>-methyl group and the C<sub>17</sub>-side-chain when the C/D ring fusion is *cis* than when it is *trans*. This may be the factor responsible for the greater stability of the *trans* isomer. In previous instances, where epimerization of steroids converted the C/D ring fusion from the *trans* to the *cis* configuration, there was usually a keto group at C<sub>11</sub> and therefore the question of eclipsing did not arise; *cf.* ref. 3c. An exception is reported by F. Sondheimer, R. Yashin, G. Rosenkranz and C. Djerassi, *THIS JOURNAL*, **74**, 2696 (1952); C. Djerassi, W. Frick, G. Rosenkranz and F. Sondheimer, *ibid.*, **75**, 3496 (1953); here the C/D *trans*-isomer is epimerized to *cis* despite the presence of a saturated side-chain at C<sub>17</sub>; *cf.* also ref. 3c.

The normally greater stability of the *cis* isomer in hydrindane systems is in contradistinction to the situation with other 1,2-disubstituted cyclohexanes where the *trans* isomer (both substituents equatorial) is more stable than the corresponding *cis* isomer (one substituent equatorial, one axial). This apparent anomaly has been explained in two different ways. Early investigators assumed that the six-membered ring in *cis*-hydrindane was in the boat form.<sup>3b,12</sup> It can be seen with the aid of molecular models that the nearly planar<sup>13</sup> five-membered ring can be *cis*-fused readily to the parallel bonds at the side of the boat-shaped six-membered ring. However, because of other unfavorable steric interactions in a boat-shaped cyclohexane ring,<sup>14</sup> such a conformation may not be energetically attractive. Angyal and MacDonald,<sup>15</sup> and, independently, L. P. Kuhn<sup>16</sup> therefore have assumed that the six-membered ring in a *cis*-hydrindane system is in the chair form. These authors point out that while in a normal (undeformed) chair *cis*-(e,a) and *trans*-(e,e) fusion should be equally facile because of the perfect staggering of the bonds, the six-membered ring in the hydrindanes may be deformed slightly, so as to bring the bonds used in the attachment of the five-membered ring closer together. Now a deformation bringing an equatorial and an axial bond together is relatively easy, but a deformation bringing two equatorial bonds together involves considerable strain. (The former type of deformation decreases the puckering of the ring, the latter increases it). Therefore the deformation favorable to *cis* fusion can be brought about much more readily than a deformation favorable to *trans* fusion. Angyal and MacDonald<sup>15</sup> have adduced evidence for the correctness of their view in the *epi*-inositol (hexahydroxycyclohexane) system. It seemed, however, that further evidence on the conformation of a *cis*-hydrindane system bearing as few extraneous substituents as possible was desirable. In the present work the reaction of vicinal diols with lead tetraacetate was used as a test reaction for the relative position of the hydroxyl groups in 5,6-disubstituted *cis*-hydrindanes.

(12) (a) H. G. Derr, *Rec. trav. chim.*, **41**, 318 (1922); (b) W. Hückel and H. Friedrich, *Ann.*, **451**, 132 (1926).

(13) J. E. Kilpatrick, K. S. Pitzer and R. Spitzer, *THIS JOURNAL*, **69**, 2483 (1947).

(14) See, for example, the excellent review by S. J. Angyal and J. A. Mills, *Rev. pure appl. chem.*, **2**, 185 (1952).

(15) S. J. Angyal and C. G. MacDonald, *J. Chem. Soc.*, 686 (1952).

(16) L. P. Kuhn, *THIS JOURNAL*, **74**, 2192 (1952).

Criegee and co-workers have investigated extensively the rate of cleavage of vicinal glycols with lead tetraacetate.<sup>17,18</sup> As the data in Table I indicate, the ratio of the rates of reaction of *cis*- and *trans*-cyclohexanediol-1,2 with lead tetraacetate is only 22.5,<sup>18</sup> but the corresponding ratio for the cyclopentanediols-1,2 is over 3,000.<sup>17</sup> Presumably this is because in both cyclohexanediols the bonds linking the hydroxyl groups form angles of 60° with each other, while in *cis*-cyclopentanediol-1,2 this angle is 0° and in *trans*-cyclopentanediol-1,2 it is 120°. (The slight difference in ease of oxidation of the diastereoisomeric cyclohexanediols may be due to the difference in ease of deformation discussed above.)

It therefore is expected that if in *cis*-hydrindane the six-membered ring were a boat, there should be a large difference in the rate of reaction of the *cis*-5,6-diol and the *trans*-5,6-diol, since in the *cis*-diol the bonds linking the hydroxyl groups make 0° angles and in the *trans* isomer they make 120° angles.<sup>19</sup> On the other hand, if the six-membered ring in *cis*-hydrindane is a chair, then the ratio of the rates of the *cis*- and *trans*-5,6-diols should be no greater than the corresponding ratio for the cyclohexane-1,2-diols.<sup>20</sup>

Because of difficulties encountered in the synthesis of the *cis*-hydrindane-5,6-diols, the corresponding 2-oxa compounds III, IV were investigated instead. The synthesis of these compounds was achieved readily as shown in the formulations.

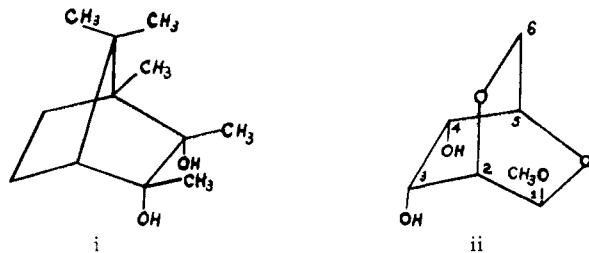
It is of interest that apparently only one of the two possible *cis* isomers was formed in the permanganate oxidation. While we have no experimental evidence as to which isomer is obtained, we believe that it is the one in which hydroxyl groups are *trans* to the ring junction. It might be noted that when the hydroxyl groups are *cis* to the ring junction, the axial hydroxyl group is seriously crowded by the axial carbon atom of the five-membered ring *meta* to it.<sup>21</sup>

The rates of reaction of compounds VIII and IX

(17) R. Criegee, E. Büchner and W. Walther, *Ber.*, **73**, 571 (1940).

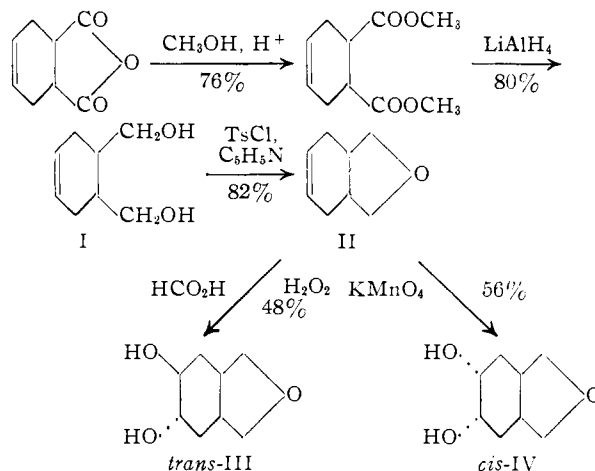
(18) R. Criegee, L. Kraft and B. Rank, *Ann.*, **507**, 159 (1933).

(19) Previous work confirms that *cis*-1,2-cyclohexanediols in which the cyclohexane ring is forced into the boat conformation by a 1,4-bridge react with lead tetraacetate very rapidly: e.g., *cis*-2,3-dimethyl-2,3-camphanediol (i)<sup>17</sup> and methyl 2,6-anhydro- $\alpha$ -D-altroside (ii)—R. E. Reeves, *THIS JOURNAL*, **72**, 1499 (1950).



(20) Actually the ratio should be somewhat less than in cyclohexane-1,2-diol. It can be seen in models that the deformation of the cyclohexane ring when *cis* fused to a cyclopentane ring—as postulated in ref. 15—will actually make the equatorial (*trans*) bonds in positions 5 and 6 approach each other somewhat, while it makes the equatorial and axial bonds (*cis*) diverge slightly. Table I indicates that this is borne out, since  $k_{cis}/k_{trans}$  is slightly but significantly smaller for the *cis*-2-oxa-hydrindane-5,6-diols than for the cyclohexane-1,2-diols.

(21) A similar case is discussed by W. S. Johnson, *Experientia*, **7**, 315 (1951), and *THIS JOURNAL*, **75**, 1498 (1953).



with lead tetraacetate in 99.5% acetic acid are shown in Table I. Corresponding rates for the cyclohexane-1,2-diols and the cyclopentane-1,2-diols also were measured; values from Criegee's work<sup>17,18</sup> are included for comparison.

TABLE I  
RATES OF REACTION OF 1,2-DIOLS WITH LEAD TETRAACETATE IN 99.5% ACETIC ACID

Compound	$T$ , °C.	$k^{cis}$	$k^{trans}$	$\frac{k_{cis}}{k_{trans}}$	Ref.
Cyclohexanediol-1,2	20	5.04	0.224	22.5	18
Cyclohexanediol-1,2	25	8.11	.316	21.5	<sup>b</sup>
Cyclohexanediol-1,2	30	16.1	.755	21.4	18
Cyclopentanediol-1,2	20	>40,000	12.8	>3000	17
Cyclopentanediol-1,2	25	<sup>c</sup>	21.4	Large	<sup>b</sup>
Cyclopentanediol-1,2	30	.....	39.4	.....	17
2-Oxa- <i>cis</i> -hydrindanediol-5,6 (III, IV)	25	5.48	0.323	17	<sup>b</sup>

<sup>a</sup>  $k$  is in lit. mole<sup>-1</sup> min.<sup>-1</sup>. <sup>b</sup> This work. <sup>c</sup> Too fast to measure.

As Table I shows, the  $k_{cis}/k_{trans}$  for the 2-oxa-*cis*-hydrindanediols-5,6 (III, IV) is actually smaller than that for cyclohexanediol-1,2. Therefore it appears that the six-membered ring in these compounds is a slightly deformed chair, as postulated by Angyal and MacDonald,<sup>15</sup> and not a boat. This conclusion is similar to that reached by Ottar<sup>22</sup> for cyclohexene oxide on the basis of X-ray diffraction data.

Independent evidence for the correctness of this view comes from a consideration of the infrared absorption frequencies of the diols in the hydroxyl region. This method, being a static one, has the advantage that complications due to changes of conformation during chemical reaction are ruled out. Kuhn<sup>16,23</sup> has found that the 1,2-cyclohexanediols show *two* hydroxyl absorption peaks in the infrared in dilute solution, one due to unbonded OH, the other due to intramolecularly hydrogen-bonded OH; these peaks are about 30–40 cm.<sup>-1</sup> apart. Because an equatorial hydroxyl is equidistant from an adjacent equatorial or axial hydroxyl, the distance between the bonded and unbonded hydroxyl peak is about the same in the two diastereoisomers. In contrast, in 1,2-cyclopentanediol the hydroxyl groups are close together in the *cis* isomer but far apart in the *trans* isomer; consequently the

(22) B. Ottar, *Acta Chem. Scand.*, **1**, 283 (1947).

(23) See also L. P. Kuhn, *THIS JOURNAL*, **76**, 4323 (1954).

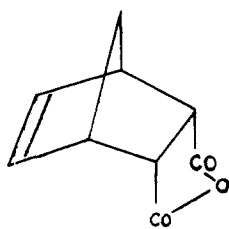
*cis* isomer shows a large distance (61 cm.<sup>-1</sup>) between the bonded and unbonded hydroxyl peak, while the *trans* isomer has no hydrogen bond at all and shows only one peak due to unbonded hydroxyl. Kuhn's data along with similar data obtained by us are summarized in Table II; this table also indicates the corresponding shift for the 2-oxahydrindanediois-5,6. Again the situation in the bicyclic system is similar to that in the chair-shaped cyclohexanediol and different from that in cyclopentane-diol which simulates the geometry of the hydroxyl groups in a boat-shaped cyclohexane ring.

TABLE II

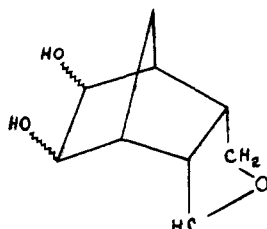
Compound	POSITION OF HYDROXYL BANDS IN THE INFRARED (CM. <sup>-1</sup> )		$\Delta\nu$	Ref.
	Free OH	Bonded OH		
<i>cis</i> -Cyclopentane-diol-1,2	3633	3572	61	16
	3635	3573	62	<sup>a</sup>
<i>trans</i> -Cyclopentane-diol-1,2	3620	None	..	16
	3624	None	..	<sup>a</sup>
<i>cis</i> -Cyclohexane-diol-1,2	3626	3587	39	16
	3623	3584	39	<sup>a</sup>
<i>trans</i> -Cyclohexane-diol-1,2	3634	3602	32	16
	3634	3602	32	<sup>a</sup>
<i>cis</i> -2-Oxahydrindane-diol-5,6 (IX)	3625	3595	30	<sup>a</sup>
<i>trans</i> -2-Oxahydrindane-diol-5,6 (VIII)	3635	3601	34	<sup>a</sup>

<sup>a</sup> This work.

For purposes of comparison we also synthesized one isomer of *endo*-4,7-endomethylene-2-oxahydrindane-*cis*-5,6-diol (V) from bicyclo[2,2,1]-heptene-*endo*-*cis*-2,3-dicarboxylic anhydride (VI) in a manner analogous to that used in transforming *cis*-



VI



V

$\Delta^4$ -tetrahydrophthalic anhydride into IV; as expected,<sup>19</sup> the rate of cleavage of V with lead tetraacetate was too fast for measurement. Attempts to prepare the *trans* isomer of V by performic acid oxidation gave a sirup which showed hydroxyl bands in the infrared, but which did not react with lead tetraacetate; it is likely that a rearrangement occurred in this reaction similar to that observed in the peracid oxidation of norbornylene.<sup>24,25</sup> Regarding the stereochemistry of compound V, it can be said with assurance that the tetrahydrofuran ring is *endo* and that the hydroxyl groups are *cis*, but there is some doubt as to whether the latter are *exo* or *endo*. The permanganate oxidation of norbornylene is known to yield the *exo*-diol,<sup>24</sup> thus by analogy one would expect V to be an *exo*-diol also. Yet the infrared spectrum of the compound, unlike that of the *cis*-diol from norbornylene,<sup>24</sup> shows three bands in the hydroxyl region—

(24) H. Kwart and W. G. Vusburgh, THIS JOURNAL, **76**, 5400 (1954).

(25) H. M. Walborsky and D. F. Loncrini, *ibid.*, **76**, 5396 (1954).

one due to unbonded OH, and two others, shifted with respect to the first by 95 and 204 cm.<sup>-1</sup>. If the less shifted band is to be ascribed to intramolecular bonding between hydroxyls (the corresponding shift in the norbornylene compound is 102 cm.<sup>-1</sup><sup>24</sup>), the more shifted one may be due to transannular hydrogen bonding between one of the hydroxyl groups and the ether oxygen, which would necessitate the *endo* configuration for compound V.

### Experimental<sup>26</sup>

*cis*-1,2,3,6-Tetrahydrophthalyl Alcohol (I).—A slurry of 30.5 g. of lithium aluminum hydride in 1000 ml. of anhydrous ether was heated under reflux for 45 minutes; then a solution of 134.5 g. of diethyl *cis*- $\Delta^4$ -tetrahydrophthalate<sup>27</sup> was added gradually and boiling was continued for 2.5 hours. The reaction mixture was decomposed by the addition of water and dilute sulfuric acid in the usual way<sup>28</sup> and then extracted continuously with ether for three days. The combined ether solutions were dried over potassium carbonate and concentrated. Crystallization of the residue from a mixture of benzene and Skellysolve B yielded 67 g. (80%) of the glycol (I), m.p. 32.5–34.5°. The product boiled at 106–107° (0.1 mm.); lit.<sup>29a</sup> 130–137° (1–1.5 mm.); 169–170° (11 mm.).

The bis-3,5-dinitrobenzoate melted at 143–144°, after crystallization from ethanol-ethyl acetate.

Anal. Calcd. for C<sub>22</sub>H<sub>18</sub>N<sub>4</sub>O<sub>12</sub>: C, 49.81; H, 3.42. Found: C, 50.06; H, 3.52.

*cis*-2-Oxa-3a,4,7,7a-tetrahydroindane (II).—The synthesis of this compound was patterned after that of the corresponding saturated compound.<sup>29</sup> To a boiling solution of 35 g. (0.25 mole) of VI in 100 ml. of dry pyridine, 47.5 g. (0.25 mole) of *p*-toluenesulfonyl chloride was added over a 20-minute period. Heating was continued for 15 minutes; then the mixture was allowed to cool and poured into a mixture of ice and 50 ml. of concentrated sulfuric acid. An oily layer precipitated and was separated. The aqueous layer was extracted once with ether, which was combined with the original organic layer and dried over potassium carbonate. Concentration of the solution followed by distillation gave 24.7 g. (82%) of 2-oxa-3a,4,7,7a-tetrahydroindane (II) boiling at 63–64° (13 mm.), *n*<sub>D</sub><sup>20</sup> 1.4884.

Anal. Calcd. for C<sub>8</sub>H<sub>12</sub>O: C, 77.37; H, 9.74. Found: C, 77.10; H, 9.89.

*cis*-2-Oxa-hydrindane-*cis*-5,6-diol (IV).—A vigorously stirred mixture of 12.8 g. of II and 125 ml. of water was cooled below 5° by means of an ice-salt mixture and a solution of 14 g. of potassium permanganate in 300 ml. of water was added to it at such a rate as to maintain the temperature at 4–5°. After all the permanganate was added, stirring was continued for 15 minutes and the mixture was left overnight. It was then filtered to remove manganese dioxide, which, in turn, was washed with 150 ml. of water. The combined filtrate and washings were extracted once with ether to remove unreacted olefin. The aqueous layer was then saturated with potassium carbonate and extracted with chloroform. Removal of the chloroform left 9 g. (56%) of glycol which, after crystallization from chloroform-Skellysolve B gave beautiful white platelets which, however, melted over a range (100–104°). Further recrystallization did not improve the melting point, but on occasion needle-shaped crystals were obtained either by themselves, or in admixture with the platelets. The plates and needles had the same melting point, did not depress each other's melting point and had the same infrared spectrum even as Nujol mulls. They appear to be either readily interconvertible polymorphs, or simply different crystalline habits of the same crystal structure.<sup>30</sup> No evidence for the formation of

(26) All melting points and boiling points are uncorrected. Microanalyses by Micro-Tech Laboratories, Skokie, Ill.

(27) A. C. Cope and E. C. Herrick, *Org. Syntheses*, **30**, 29 (1950).

(28) W. G. Brown, in R. Adams, "Organic Reactions," Vol. 6, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 486.

(29a) J. E. Ladburg and E. E. Turner, *J. Chem. Soc.*, 3885 (1954); W. J. Bailey and J. Rosenberg, THIS JOURNAL, **77**, 73 (1955).

(29) G. A. Haggis and L. N. Owen, *J. Chem. Soc.*, 389 (1953).

(30) *cis*-Cyclohexane-diol-1,2 is reported to exist in three polymorphic forms; ref. 12a.

two epimeric glycols was obtained either in the recrystallization or by chromatography.

*Anal.* Calcd. for  $C_8H_{14}O_3$ : C, 60.73; H, 8.92. Found: C, 60.11; H, 8.82.

The bis-3,5-dinitrobenzoate melted at 195–197° after crystallization from ethanol-ethyl acetate.

*Anal.* Calcd. for  $C_{22}H_{18}N_4O_{13}$ : C, 48.36; H, 3.32. Found: C, 48.57; H, 3.38.

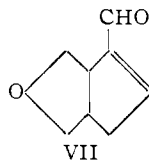
*cis*-2-Oxa-hydrindane-*trans*-5,6-diol (III).—To a well-stirred solution of 24 ml. of 30% hydrogen peroxide in 100 ml. of 90% formic acid initially at room temperature was added dropwise 20.9 g. (0.168 mole) of II. The temperature was kept below 40° by means of a cold water-bath. After all the olefin had been added, stirring was continued for 3.5 hours and the mixture was then left overnight. As much formic acid as possible was distilled at the vacuum of an aspirator and a temperature not exceeding 60°. A solution of 20 g. of sodium hydroxide in 40 ml. of water then was added gradually with some cooling (temperature below 45°) and the mixture was immersed in a water-bath at 45° for 15 minutes to effect hydrolysis of esters. It was then extracted repeatedly with 200–300 ml. portions of chloroform. Removal of the chloroform left 12.85 g. (48%) of crude glycol which, after three recrystallizations from chloroform-Skellysolve B, melted at 130–132°.

*Anal.* Calcd. for  $C_8H_{14}O_3$ : C, 60.73; H, 8.92. Found: C, 60.33; H, 8.86.

The bis-3,5-dinitrobenzoate melted at 196–198° after crystallization from ethanol-ethyl acetate.

*Anal.* Calcd. for  $C_{22}H_{18}N_4O_{13}$ : C, 48.36; H, 3.32. Found: C, 48.57; H, 3.30.

**Cleavage of *cis*-2-Oxa-hydrindane-*cis*-5,6-diol.**—A solution of 2 g. of the *cis*-diol IV was added to a solution of 6 g. of lead tetraacetate in 2.0 ml. of glacial acetic acid at 34°. After one-half hour, there was no further consumption of tetraacetate, as indicated by titration. The acetic acid was neutralized with saturated sodium carbonate solution and the suspension extracted with 300 ml. of chloroform. Concentration of the chloroform solution left a viscous residue which was converted to its 2,4-dinitrophenylhydrazone.<sup>31</sup> A total of 3.7 g. of the derivative was obtained by first allowing it to crystallize and then diluting the mother liquor with water. After two crystallizations, from ethanol-ethyl acetate and absolute ethanol, the derivative melted at 204–205°. Analysis indicated it to be the 2,4-dinitrophenylhydrazone of the cyclic unsaturated aldehyde VII.



*Anal.* Calcd. for  $C_{14}H_{14}N_4O_6$ : C, 52.83; H, 4.43. Found: C, 52.82; H, 4.37.

**Other Glycols.**—*cis*-Cyclohexanediol-1,2, obtained by permanganate oxidation of cyclohexene, melted at 97–99° (lit.<sup>32</sup> 98.4–99.2°). The *trans* isomer<sup>33</sup> melted at 102–104.5° (lit.<sup>33</sup> 101.5–103°). *cis*-Cyclopentanediol-1,2, obtained by permanganate oxidation of cyclopentene, was a liquid, b.p. 103° (13 mm.),  $n_D^{25}$  1.4761. The literature has reported this compound both as a liquid,<sup>34</sup> b.p. 88–92° (2 mm.),  $n_D^{25}$  1.4770, and as a low-melting solid,<sup>32</sup> m.p. 29.8–30.5°, b.p. 105–106° (10 mm.). The *trans* isomer, obtained by oxidation of cyclopentene with performic acid,<sup>34</sup> boiled at 103–104° (2 mm.) and solidified at 52°. Owen<sup>34</sup> reports b.p. 93° (2 mm.), m.p. 50°; Verkade<sup>32</sup> found b.p. 101° (1.5 mm.), m.p. 53.7°.

The diol V was obtained from the anhydride VI by a method analogous to that described above for the conversion of tetrahydrophthalic anhydride to the diol IV. The dimethyl ester corresponding to VI boiled at 141–142° (13

(31) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

(32) P. E. Verkade, *et al.*, *Ann.*, **467**, 221 (1928).

(33) A. Roebuck and H. Adkins, *Org. Syntheses*, **28**, 35 (1948).

(34) L. N. Owen and P. N. Smith, *J. Chem. Soc.*, 4026 (1952).

mm.),  $n_D^{25}$  1.4836; lit.<sup>35,36</sup> b.p. 129–130° (9 mm.),  $n_D^{20}$  1.4852. Reduction with lithium aluminum hydride gave the corresponding dimethylol compound,<sup>36</sup> m.p. 84–87° (lit.<sup>36a</sup> 86°) in 84% yield. This was cyclized to the corresponding furan in 82% yield; the product melted at 91° after sublimation but resisted purification to analytical purity. It was oxidized to V by means of potassium permanganate in 32% yield. The glycol V melted at 71–72° after crystallization from chloroform-Skellysolve B from which it separated in long needles.

*Anal.* Calcd. for  $C_9H_{14}O_3$ : C, 63.51; H, 8.29. Found: C, 63.67; H, 8.33.

The rate of cleavage of V with lead tetraacetate was too fast for measurement (reaction virtually complete after 25 seconds). The infrared spectrum of X showed a sharp peak at 3629  $cm^{-1}$  and somewhat broader peaks at 3534 and 3425  $cm^{-1}$ .

TABLE III  
TYPICAL VARIATIONS OF  $k$

Time, min.	$S_2O_8^{2-}$ , ml.	Ratio <sup>a</sup>	$a - x$	$x$	$k$
Compound III, initial concentration of reagents 0.0125 M					
0.0	27.90	1.000	0.0125	0.0000	...
5.0	27.26	0.977	.0122	.0003	0.380
15.0	26.45	.948	.0118	.0007	.292
30.0	24.75	.887	.0111	.0014	.340
50.0	23.05	.822	.0103	.0022	.340
133.0	17.70	.631	.0079	.0046	.350
165.0	16.25	.582	.0073	.0052	.344
					Average 0.341 ± 0.018

Compound IV, initial concentration of reagents 0.0125 M					
0.0	24.85	1.000	0.0125	0.0000	..
4.0	19.38	0.779	.0097	.0028	5.77
9.0	15.15	.613	.0077	.0048	5.54
15.0	12.08	.486	.0061	.0064	5.59
23.0	9.39	.378	.0048	.0077	5.59
35.0	7.04	.280	.0035	.0089	5.77
					Average 5.65 ± 0.09

<sup>a</sup> Ratio of final to initial titer.

TABLE IV  
AVERAGE RATE CONSTANTS FROM VARIOUS RUNS

Compound	Concn., M	Lead tetraacetate concn., M	$k$
<i>cis</i> -Cyclohexanediol-1,2	0.0050	0.0050	7.93 ± 0.08
	.0125	.0125	8.29 ± 0.07
	Average		8.11
<i>trans</i> -Cyclohexanediol-1,2	0.0050	0.0050	0.314 ± 0.042 <sup>a</sup>
	.0125	.0125	0.376 ± 0.003
<i>trans</i> -Cyclopentanediol-1,2	0.0125	0.0125	21.04 ± 0.17
	IV ( <i>cis</i> )	.0050	.0050
IV ( <i>cis</i> )	.0135	.0125	5.65 ± .09
	.00625	.0125	5.48 ± .12
	Average		5.48
III ( <i>trans</i> )	0.0050	0.0050	0.288 ± 0.021 <sup>a</sup>
	.0125	.0125	.341 ± .014
	.00835	.0167	.305 ± .012
Average		.323	

<sup>a</sup> These values were not taken into consideration in the averages because of the large errors and because of drift in the kinetic run.

(35) M. S. Morgan, *et al.*, *THIS JOURNAL*, **66**, 404 (1944).

(36) (a) K. Alder and W. Roth, *Ber.*, **87**, 161 (1954); (b) W. J. Bailey and W. B. Lawson, *THIS JOURNAL*, **77**, 1606 (1955).

**Kinetic Runs.**—Weighed amounts of the glycols were dissolved in 99.5% acetic acid.<sup>37</sup> Lead tetraacetate solutions were prepared weekly by dissolving the requisite amount of the solid in 99.5% glacial acetic acid<sup>12</sup> and were titrated immediately before use. The solutions were thermostated at 25° (fluctuation less than 0.1°) for one hour, then mixed. Aliquots were withdrawn at periodic intervals and quenched by running them into 100 ml. of a solution 0.15% in sodium iodide and 0.5% in sodium acetate. The iodine liberated was then back-titrated with 0.001 *N* thiosulfate solution.

Several runs were made for compounds III and IV, both with equal and unequal initial concentrations of glycol and lead tetraacetate. As observed by Criegee,<sup>18</sup> the kinetics

(37) Since slight variations of the concentration of water in the acetic acid affect the rates considerably—R. Criegee and E. Büchner, *Ber.*, **73**, 563 (1940)—the same stock solution of acetic acid was used throughout this work.

is clearly second order (order one in glycol and in tetraacetate). Table III summarizes typical variations of *k* within two individual runs. Table IV compares average constants from different runs. The average of the values for each compound in Table III is listed in Table I. Some of the faster reactions (*cis* isomers) were followed up to 70% completion, the slower runs (*trans* isomers) up to 40% completion.

**Infrared Spectra.**—The infrared spectra reported in Table II were recorded on a Perkin-Elmer double beam instrument equipped with a calcium fluoride prism.<sup>38</sup> Solutions of compounds III and IV in carbon tetrachloride were saturated. Solutions of the cyclopentenediols and cyclohexanediols in carbon tetrachloride were diluted until a convenient intensity of absorption was observed. All solutions were seen through a 1-cm. quartz cell.

(38) We are indebted to Mr. George Svatos for these determinations. NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH DAKOTA]

## Diaryl Bis-(cyclopentadienyl)-titanium Compounds<sup>1</sup>

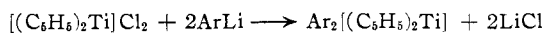
BY LAWRENCE SUMMERS, ROBERT H. ULOTH AND ANN HOLMES

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Reaction of bis-(cyclopentadienyl)-titanium dichloride with the appropriate aryllithium compound produced diaryl bis-(cyclopentadienyl)-titanium derivatives, Ar<sub>2</sub>[(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti] (where Ar = aryl). The diphenyl-, di-*m*-tolyl-, di-*p*-tolyl- and di-*p*-dimethylaminophenyl compounds were obtained as crystalline substances with varying thermal stabilities. Attempts to isolate the di-*o*-tolyl or di-*α*-naphthyl derivatives were unsuccessful.

Bis-(cyclopentadienyl)-iron<sup>2</sup> represents a new type of non-benzenoid aromatic system,<sup>3</sup> and several investigations of the organic chemistry of this complex have been reported.<sup>3,4</sup> From another point of view, these "penetration" or "sandwich" complexes of transition metals may be regarded as being themselves of the nature of metals, and their properties in this respect may be investigated.<sup>5</sup> In connection with our program of research on organometallic chemistry, we have considered such complexes from this latter point of view, and have investigated the possibility that they would form "organometallic" derivatives in which the complex itself would act like a central metal. The preparation and properties of diaryl derivatives of bis-(cyclopentadienyl)-titanium(IV) were mentioned in a preliminary communication.<sup>6</sup> The present paper presents the experimental data pertaining to these preparations.

The diaryl bis-(cyclopentadienyl)-titanium compounds were prepared by reaction of bis-(cyclopentadienyl)-titanium dichloride with aryllithium solutions in diethyl ether.



In general the use of chlorides rather than bromides in such preparations is advantageous, because the

(1) This work was carried out under contract Nonr-582(00) with the Office of Naval Research.

(2) T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

(3) R. B. Woodward, M. Roseblum and M. C. Whiting, *THIS JOURNAL*, **74**, 3458 (1952).

(4) See for instance P. L. Pauson, *ibid.*, **76**, 2187 (1954); R. A. Benkeser, D. Goggin and G. Schroll, *ibid.*, **76**, 4025 (1954).

(5) For leading references on bis-(cyclopentadienyl) complexes of various transition metals, see especially recent publications of G. Wilkinson and others in *THIS JOURNAL* and of E. O. Fischer and others in *Z. Naturforsch.*

(6) L. Summers and R. H. Uloth, *THIS JOURNAL*, **76**, 2278 (1954).

lithium chloride formed then precipitates out immediately. Lithium bromide may tend to remain in solution in the diethyl ether, and to complicate the preparation. The bis-(cyclopentadienyl)-titanium dichloride was prepared from titanium tetrachloride and cyclopentadienyllithium. The latter was obtained by reaction of cyclopentadiene with *n*-butyllithium, which in turn was made from *n*-butyl chloride and lithium in an alkane solvent. Since the *n*-butyllithium solution was to be refluxed with cyclopentadiene, the presence of diethyl ether was avoided in this step, because warm diethyl ether reacts with alkyllithium compounds.

The technique described avoids the presence of more than one kind of halogen in the reaction mixtures. If more than one halogen is present, uncertainty arises as to the composition of the bis-(cyclopentadienyl)-metal halide. (In one case, for example, cyclopentadienyllithium was prepared from cyclopentadiene and phenyllithium which had been prepared as usual from bromobenzene and lithium in diethyl ether. When this cyclopentadienyllithium was treated with zirconium tetrachloride, the product was bis-(cyclopentadienyl)-zirconium dibromide, and not the dichloride.<sup>7</sup>) In such cases, saturation of the reaction mixture with the appropriate hydrogen halide has been used as a means of assuring conversion to the desired product.<sup>8</sup> The use, in such preparations, of cyclopentadienylsodium prepared from cyclopentadiene and sodium<sup>8</sup> would avoid some of these complications.

For the preparation of the diaryl bis-(cyclopentadienyl)-titanium, an aryllithium solution which could be prepared in diethyl ether, since aryllithium

(7) L. Summers and R. H. Uloth, unpublished data.

(8) G. Wilkinson and J. M. Birmingham, *THIS JOURNAL*, **76**, 1281 (1954).