THE OXYMERCURATION OF 1,4-↑↑-METHYLENE-Δ⁵-CYCLOHEXENE-2-CARBOXYLIC ACIDS

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ABSTRACT

The oxymercuration of 1,4- \uparrow -methylene- Δ^{5} -cyclohexene-2- \uparrow -carboxylic acid yields two diastereomeric hydroxychloromercurials. Their configurations cannot be specified on the basis of information now available with certainty. The oxymercuration of 1,4- \uparrow -methylene- Δ^{5} -cyclohexene-2- \downarrow -carboxylic acid also yields two diastereomers, which are designated as $6-\downarrow$ -hydroxy- $5-\downarrow$ -chloromercuri-1,4- \uparrow -methylenecyclohexane-2- \downarrow -carboxylic acid, γ -lactone and $6-\downarrow$ -hydroxy- $5-\uparrow$ -chloromercuri-1,4- \uparrow -methylenecyclohexane-2- \downarrow -dicarboxylic acid, γ -lactone because the former is more easily deoxymercurated than the latter and because their dipole moments match relatively the corresponding moments of the analogous dicarboxylic acid γ -lactones, the configurations of which have been proved chemically. This is the first instance where two diastereomers of opposite configuration have been shown to be formed in an oxymercuration.

During a recent study of the oxymercuration of various substituted [2.2.1]-bicycloheptenes (1) an anomaly has become apparent. The [2.2.1]-bicycloheptenes behave differently from other cyclic alkenes because the oxymercuration is acid catalyzed and the oxymercurials have the $\uparrow\downarrow$ (trans) configuration. The exception is the isolable oxymercurial III-C from 1,4- $\uparrow\uparrow$ -methylene- Δ^5 -cyclohexene-2,3- $\downarrow\downarrow$ -dicarboxylic acid. The chemical behavior of III-C shows it to be 5- \downarrow -hydroxy-6- \downarrow -chloromercuri-1,4- $\uparrow\uparrow$ -methylene-cyclohexane-2,3- $\downarrow\downarrow$ -dicarboxylic acid, γ -lactone. But if the reaction proceeds through an ionic intermediate, at least one other diastereomer (probably 5- \downarrow -hydroxy-6- \uparrow -chloromercuri-1,4- $\uparrow\uparrow$ -methylenecyclohexane-2,3- $\downarrow\downarrow$ -dicarboxylic acid, γ -lactone, IV-C, ought to be formed. However, this diastereomer, IV-C, has the same solubility characteristics as III-C. Its main chemical difference from III-C, a higher resistance toward deoxymercuration, would not be apparent if it were a contaminant of low concentration. Consequently its presence in small-amount might be missed, especially if traces of other diastereomers were present.



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For this reason we decided to study the oxymercuration of a simpler substance, $1,4-\uparrow\uparrow$ -methylene- Δ^5 -cyclohexane-2- \downarrow -carboxylic acid, I. Since this acid is obtained from pentadiene and acrylic acid (2) in difficultly separable admixture with $1,4-\uparrow\uparrow$ -methylene- Δ^5 -cyclohexene-2- \uparrow -carboxylic acid, IV, we have first effected a separation by an oxymercuration of the mixture. Fractional crystallization of the products of oxymercuration leads mainly to two oxymercurials which, when deoxymercurated by means of hydrochloric acid, regenerate I and IV separately. The ratio of $2-\downarrow$ - to $2-\uparrow$ -carboxylic acids in the mixture has been found by this method to be 12-13 to 1, thus more in agreement with the 9:1 ratio found by infrared analysis (3) than with the 77:23 ratio reported (4) by separation of I as its iodolactone.

We have treated $1,4-\uparrow\uparrow$ -methylene- Δ^5 -cyclohexene-2- \downarrow -carboxylic acid, I, in water with mercuric acetate, then with sodium chloride, and have obtained a crude 83% yield of mercurials m.p. 183–195°. When this mixture is fractionally crystallized the overall yield is found to be comprised of 77% of one mercurial and 3% of another, the remaining 3% being either more of the major product or else a yet unisolated isomer. We have assigned to the major product, III, the stereo-structure 6- \downarrow -hydroxy-5- \downarrow -chloromercuri-1,4- $\uparrow\uparrow$ -methylenecyclohexane-2- \downarrow -carboxylic acid, γ -lactone.

During the progress of the present investigation the oxymercuration of I was reported by Henbest and Nicholls (5), who assigned to their sole product (identical with our major product) the structure 6- \downarrow -hydroxy-5- \uparrow -chloromercuri-1,4- $\uparrow\uparrow$ -methylenecyclohexane-2- \downarrow carboxylic acid, γ -lactone, IV, which we consider to be that of our minor product.

When our major product is treated in methanol with hydrazine a mixture is obtained consisting of 1,4- $\uparrow\uparrow$ -methylenecyclohexane-2- \downarrow -carboxylic acid and the mercurial which we specify as IV. Either of III or IV may be reduced by use of sodium borohydride (1, 5) to 6- \downarrow -hydroxy-1,4- $\uparrow\uparrow$ -methylenecyclohexane-2- \downarrow -carboxylic acid, γ -lactone, V (6). The difference between the two mercurials must then rest entirely with the $\downarrow\downarrow$ versus $\downarrow\uparrow$ relationship of hydroxy and chloromercuri groups. Thus the expectation that acidcatalyzed oxymercuration ought to give more than one product has been realized.

On the basis of chemical reaction the assignment by Henbest and Nicholls is entirely arbitrary. These authors rely factually on the results of an X-ray diffraction study carried out earlier in our laboratory which has since been thought to be non-definitive (1). On the other hand our structure specifications are based on the observation that our minor product is more difficult to deoxymercurate than is our major product. Since the minor product also has a higher dipole moment than the major product we believe that our assignments (major product, III, and minor product, IV) are correct, because of these correlations with proven configurations among the mercurials from the $1,4-\uparrow\uparrow$ -methylene- Δ^5 -cyclohexenedicarboxylic acids (7). Comparison in respect of dipole moment is shown in Table I. The dicarboxylic analogues are in each instance designated by the suffix "C".

The mechanism of oxymercuration for I is assumed to be the same as that for $1,4-\uparrow\uparrow$ -methylene- Δ^5 -cyclohexene- $2,3-\downarrow\downarrow$ -dicarboxylic acid, I-C (1). Although oxymercuration in [2,2,1]-bicycloheptenes is expected to proceed via a mercurinium-ion type of intermediate, II, and thus ought to lead chiefly to IV, the presence of the \downarrow -carboxylic group may be expected to alter this expectation by preference to an intramolecular addition which would proceed via the undissociated salt, VII. In the absence of external ion attack the major product would be III, similar to formation of III-C from I-C.

We were unable to oxymercurate $1,4-\uparrow\uparrow$ -methylene- Δ^5 -cyclohexene-2- \uparrow -carboxylic acid, VI, in purely aqueous medium because of product contamination with the mercuric salt of VI but we have successfully isolated two hydroxy-chloromercuri- $1,4-\uparrow\uparrow$ -methylene-

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TABLE I

Comparison of dipole moments of 1,4-[↑]-methylenecyclohexane (BCH) carboxylic acids and their hydroxychloromercuri derivatives in dioxane at 20°

Compound	μ (D)
BCH-2-↓-carboxylic acid	1.65
BCH-2,3-↓↓-dicarboxylic acid, I-C	2.78^{*}
BCH-2-↑-carboxylic acid	1.61
BCH-2,3-↓↑-dicarboxylic acid, VI-C	2.49^{*}
6- \downarrow -Hydroxy BCH-2- \downarrow -carboxylic acid, γ -lactone, V	4.70^{+}
6- \downarrow -Hydroxy BCH-2,3- \downarrow \downarrow -dicarboxylic acid, γ -lactone, V-C	4.85^{*}
6-J-Hydroxy-5-J-chloromercuri BCH-2-J-carboxylic acid, γ -lactone, III	3.39
6- \downarrow -Hydroxy-5- \downarrow -chloromercuri BCH-2,3- \downarrow \downarrow -dicarboxylic acid, γ -lactone, III-C	3.88^{*}
6-J-Hydroxy-5-1-chloromercuri BCH-2-J-carboxylic acid, γ -lactone, IV	6.99
6- \downarrow -Hydroxy-5- \uparrow -chloromercuri BCH-2,3- \downarrow \downarrow -dicarboxylic acid, γ -lactone, IV-C	7.18*
?-Hydroxy-?-chloromercuri-BCH-2-1-carboxylic acid, IX	4.92
5-↑-Hydroxy-6-↓-chloromercuri BCH-2-↓-3-↑-dicarboxylic acid, C	4.75^{*} ‡

*Checks value by Kwart and Kaplan (H. Kwart and L. Kaplan. J. Am. Chem. Soc. 76, 4078 (1954)).
*Compound XXIV, p. 1338, ref. 1.



cyclohexane-2-⁺-carboxylic acids, VIII and IX, by inclusion of 2,5-dioxahexane into the reaction system. The ratio of high-melting (VIII) to low-melting diastereomer (IX) is 4:1. Unfortunately we have not found any chemical reaction by which we can specify either position or configuration for the added groups. The deoxymercuration of VIII is somewhat slower than that of IX. However, no definitive assignment of configuration can be made for them or for the 5-hydroxy-1,4- \uparrow -methylenecyclohexane-2- \uparrow -carboxylic acids obtained from them by reduction with sodium borohydride.

One may expect from consideration of the moments of the mercury-free mono- and di-carboxylic acids at the top of Table I that the values for the present pair of bicycloheptane-1-monocarboxylic acid oxymercuration derivatives will be more meaningful than those obtained for the dicarboxylic acid derivatives (1). For the latter series, an artifically low C—COOH moment (1.2 D) had to be chosen, as would be expected because of mutual rotation interaction of the two carboxyl groups. By contrast, the moments of the bicycloheptanemonocarboxylic acids are approximate to those of many alkanecarboxylic acids, and they differ only by the contribution to polarity from the norbornane ring (1).

No such disparity is to be expected between $6 \downarrow$ -hydroxy-1,4- \uparrow -methylenecyclohexane-2- \downarrow -carboxylic acid, γ -lactone and the analogue with a carboxyl group in the 3-position. Since the latter group is the only rotator, it is to be expected that $6-\downarrow-hydroxy-1,4-\uparrow\uparrow$ methylenecyclohexane-2,3- \downarrow -dicarboxylic acid, γ -lactone would differ from its carboxylicfree analogue, V, only by the vectorial component due to this rotating carboxylic group. This expectation is confirmed in fact (Table I) by comparison of the moments of V and V-C.

Despite the small difference between μ for V-C and V it is to be expected that analysis of structure V should be less complicated than that of V-C.

This may be seen in the vector model:



A slightly different set of bond moments and O—C=O bond angle than the one used for the comparable calculation of the 3- \downarrow -carboxy analogue (1) has been assumed. When the O—C=O group moment resultant (2.54 D) is assumed to be directed 84° from the *y*-axis a close correlation with the observed value is obtained.

$$\mu_{z} = 0.4 \cos^{2} 18^{\circ} + 0.8 \cos^{2} 18^{\circ} + 2.54 \cos 30^{\circ} + 0.45 = 3.735 \text{ D}$$

$$\mu_{x} = 0.4 \cos^{2} 18^{\circ} - 0.8 \cos^{2} 18^{\circ} + 2.54 \cos 119^{\circ} = -0.88 \text{ D}$$

$$\mu_{y} = 0.8 \sin^{2} 18^{\circ} - 0.4 \sin^{2} 18^{\circ} + 2.54 \sin 84^{\circ} = 2.64 \text{ D}$$

$$\mu_{r}^{2} = \mu_{z}^{2} + \mu_{x}^{2} + \mu_{y}^{2}$$

$$\mu_{r} = 4.66 \text{ D}$$

found: $\mu = 4.70 \text{ D}$

In order to calculate the moments of the two diastereomeric chloromercuri-1,4- \uparrow methylenecyclohexane-2- \downarrow -carboxylic acid, γ -lactones III and IV one must add vectorially to the coordinate moments calculated above the Cl—Hg—C group, for which an angle of 96° is assumed in the present calculation. Then a Cl—Hg moment of 3.4 D is derived from the moment of *n*-propylmercuric chloride (3.70 D) by application of the 96° C—Hg—Cl angle and a C—Hg moment of 1.3 D (1).

The moment of $6-\downarrow$ -hydroxy-5- \downarrow -chloromercuri-1,4- $\uparrow\uparrow$ -methylenecyclohexane-2- \downarrow -carboxylic acid, γ lactone, III, has been calculated on the assumption that free rotation of the chloromercuri group is impossible, with this group diametrically opposed to the carbonyl group of the lactone. This assumption seems to be reasonable on the basis of the calculation for the carboxyl analogue of III with chloromercuri at the four quadrant positions (1).

 $\mu_{z} = 3.735 - 1.3 \cos 18^{\circ} + 3.41 \cos 78^{\circ}$ $\mu_{x} = -0.880 - 1.3 \cos 72^{\circ} \cos 18^{\circ} + 3.41 \cos 12^{\circ} \cos 60^{\circ}$ $\mu_{y} = 2.64 + 1.3 \cos^{2} 72^{\circ} - 3.41 \cos 12^{\circ} \cos 30^{\circ}$ $\mu_{r} = 3.42 \text{ D} \qquad \qquad \text{found: } 3.39 \text{ D}$

This calculation gives a moment value close to that actually determined in dioxane solution at 20° .

The test of the significance of this agreement between calculated and found values for III should be the application of the same parameters to the moment calculation of the diastereomer IV, although, in the absence of hindrance in this isomer, one should assume free rotation of the chloromercuri group. This rotation has been included by calculation of the two modes, 180° removed, of chloromercuri in the plane which includes the z-axis and the 2,5-positions of the norbornane skeleton.

Mode A: $\mu_z = 3.735 + 1.3 \cos 72^\circ + 3.41 \cos 78^\circ$

 $\mu_x = -0.88 + 1.3 \cos^2 18^\circ - 3.41 \cos 12^\circ \sin 60^\circ$ $\mu_y = 2.64 + 1.3 \cos 18^\circ \cos 72^\circ + 3.41 \cos 12^\circ \cos 60^\circ$ $\mu_r = 7.23 \text{ D}$

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Mode B:
$$\mu_z = 3.735 + 1.3 \cos 72^\circ - 3.41 \cos 78^\circ$$

 $\mu_x = -0.88 + 1.3 \cos^2 18^\circ - 3.41 \cos 12^\circ \cos 30^\circ$
 $\mu_y = 2.64 + 1.3 \cos 18^\circ \cos 72^\circ + 3.41 \sin 30^\circ \cos 12^\circ$
 $\mu_r = 6.36 D$

The mean of these two resultant moments $[(52.2+40.5)/2]^{\frac{1}{2}}$ is 6.81 D, in reasonable agreement with the experimental value, 6.99 D. It may be noted that the discrepancy (0.18 D) is the same as was observed for the carboxy analogue of IV (1). This discrepancy may still be attributed to a slight obstruction to free rotation.

EXPERIMENTAL

Physical Constants

Dielectric constants of solids and solutions were determined as described previously (8). Melting points have been corrected against reliable standards (9). X-Ray diffraction patterns have been made with Cu K_{α} (Ni filtered) radiation and are expressed as relative intensities (I/I_1) for d spacings in Angstroms.

Separation of endo- and exo-1,4-Methylene-D⁵-cyclohexene-2-carboxylic Acids by Oxymercuration

A. Endo Acid

To a suspension of 28.0 g (0.2 mole) of the diastereomeric mixture of acids (2), m.p. -13° C, d_4^{25} 1.071, n_D^{20} 1.4850, in 500 ml of water was added 64.0 g (0.2 mole) of mercuric acetate. After 1 hour of stirring the system was treated with a slight excess of aqueous sodium chloride. The curdy precipitate, filtered, washed thrice with water, and dried, weighed 72 g (96%), m.p. 178–196° C. It was dissolved in a slight excess of cold 5% aqueous sodium hydroxide except for a small amount of yellow precipitate. After filtration the system was neutralized with 0.5 ml of 1% hydrochloric acid and then saturated with gaseous carbon dioxide. The precipitate, filtered, water-washed, and dried, melted at 195–200° C, 50 g. This precipitate was extracted with a mixture of dioxane and acetone (1:4) to leave 24 g, m.p. 217–219° C. Two crystallizations from the dioxane–acetone mixture left 22 g, m.p. 222–223° C.

This pure chloromercurial was deoxymercurated by warming for 3 minutes at 50° C a suspension of 23.9 g (0.064 mole) in 80 ml of methanol with 12.5 ml (0.13 mole) of conc. hydrochloric acid. The system, which was homogeneous within 15 minutes, was chilled after 1 hour and made alkaline (pH 8.3–10). The mercuric oxide was filtered off (13.6 g, 98.6%) and the filtrate was vacuum evaporated to remove the methanol. The aqueous residue was acidified to pH 3–4 and then was extracted with diethyl ether. Evaporation of the dried extract left 8 g of oil which, when crystallized at -30° C after solution in 30 ml petroleum ether (b.p. 40–60° C), gave 7.0 g (81%) of m.p. 41–42° C. Recrystallization from the same solvent raised this melting point to 44.3–45.0° C. The *p*-phenylphenacyl derivative melted at 134.9–135.4° C (9).

B. Exo Acid

The original liquor from which the oxymercurial m.p. $222-223^{\circ}$ C was precipitated was combined with the crystallization liquors and was fractionally evaporated to yield crops of successively decreasing purity which still were mainly the oxymercurial m.p. $222-223^{\circ}$ C. Final evaporation left 4.0 g, m.p. $160-178^{\circ}$ C, which was crystallized from acetonitrile (10 ml/g) to give 3.0 g (6%) of mercurial m.p. $172-172.4^{\circ}$ C.

Deoxymercuration of this mercurial by the procedure outlined above gave a 75% yield of impure 1,4- $\uparrow\uparrow$ -methylene- Δ^{5} -cyclohexene-2- \uparrow -carboxylic acid m.p. 35–37° C. Crystallization from petroleum ether (b.p. 40–60° C) raised this melting point to 38–38.5° C. Although it gave the proper *p*-phenylphenacyl derivative (m.p. 131.5–132.2° C) (3) it was still impure. The separation of this exo acid from the diastereomeric mixture is much more satisfactorily accomplished via the iodolactone (4), especially if a mixture of diastereomeric rich in exo acid is used. Actually such a mixture yielding 54% of 1,4- $\uparrow\uparrow$ -methylene- Δ^{5} -cyclohexene-2- \uparrow -carboxylic acid b.p. 87–95° C (0.01–0.2 mm), m.p. 42–44° C was obtained by alkaline saponification of the 2-cyanonorbornene mixture prepared according to Bruson (10).

Hydroxymercuration of $1,4-\uparrow\uparrow$ -Methylene- Δ^{5} -cyclohexene-2- \downarrow -carboxylic Acid

To a stirred suspension of 9.0 g (0.067 mole) of the unsaturated endo acid in 100 ml of water was added 25.6 g (0.08 mole) of mercuric acetate in small amounts during 15 minutes. After 2 hours of subsequent stirring the system was treated with a slight excess of aqueous sodium chloride. The white precipitate was dissolved in a slight excess of 10% aqueous sodium hydroxide.

After filtration to remove mercuric oxide the system was neutralized by addition of two drops of 5% hydrochloric acid and by saturation with gaseous carbon dioxide. The precipitate was filtered off and washed successively with 5% aqueous acetic acid, water, acetone, and ether; dried weight 21 g (83%), m.p. 183–195° C.

This mixture was dissolved in 1500 ml of boiling dioxane. After filtration to remove 0.45 g of mercurous salt the solution was concentrated under reduced pressure in steps to yield crystal crops weighing 12.95 g,

m.p. 217–219° C. The final mother liquor (250 ml) was vacuum-evaporated to dryness. The residue (4.2 g, m.p. 167–180° C) was dissolved in 150 ml of hot methanol and this solution was concentrated to a volume of about 120 ml whereby 3.25 g more, m.p. 217–220° C, was obtained. The mother liquor was processed as described below.

The combined crops of crude 6- \downarrow -hydroxy-5- \downarrow -chloromercuri-1,4- \uparrow -methylenecyclohexane-2- \downarrow -carboxylic acid, γ -lactone, III, m.p. 217–220° C, 16.35 g (77%), were crystallized from 4:1 methanol-dioxane mixture (50 ml/g) to melt at 222–223° C. Anal. Calc. for C₈H₉O₂HgCl: C, 25.7; H, 2.41. Found: C, 25.9; H, 2.50.

The infrared spectrum (potassium chloride pellets at 20,000 p.s.i., 24° C) is expressed in wave numbers versus extinction as follows: (716) 6.80; (746) 6.85; (788) 6.94; (842) 7.88; (878) 4.85; (888) 7.71; (900) 8.86; (950) 12.7; (986) 23.9; (1010) 9.53; (1061) 7.88; (1100) 10.9; (1128) 6.75; (1146) 12.3; (1190) 22.6; (1242) 9.46; (1272) 9.60; (1304) 17.3; (1352) 15.0; (1450) 6.35; (1564) 3.79; (1768) 20.0; (1852) 3.65; (1930) 3.10; (1982) 2.95; (2580) 4.79; (2900) 8.42; (3010) 14.2.

The X-ray diffraction pattern was [10] 12.99, [8] 9.55, [7] 2.36, [6] 4.17, [5] 3.69, [4] 3.88, [3] 5.34, [2] 2.03, [1] 6.75.

The final mother liquor from which this crude chloromercurial was isolated yielded upon final vacuum evaporation 0.58 g, m.p. 184–186° C (3%). Crystallization from ethanol (80 ml/g) raised this melting point to 186.5–187° C. Anal. Calc. for C₈H₉O₂HgCl: C, 25.7; H, 2.41. Found: C, 25.8; H, 2.46. The X-ray diffraction pattern of this 6- \downarrow -hydroxy-5- \uparrow -chloromercuri-1,4- \uparrow -methylenecyclohexane-2- \downarrow -carboxylic acid, γ -lactone (IV) was [10] 9.06, [8] 3.14, [6] 4.88, [5] 2.84, [4] 4.50, [3] 5.26, [2] 4.58, [1] 2.36.

The infrared spectrum prepared and described as above is: (722) 31.4; (750) 13.8; (788) 10.6; (816) 7.96; (840) 14.8; (888) 25.0; (938) 13.9; (960) 13.2; (979) 56.7; (1010) 47.6; (1088) 45.2; (1138) 20.0; (1150) 14.7; (1192) 53.2; (1228) 11.2; (1248) 24.5; (1274) 15.9; (1300) 28.0; (1318) 25.5; (1344) 47.3; (1452) 14.1; (1470) 10.3; (1554) 7.52; (1758) 54.7; (2290) 16.5; (3020) 40.2.

This product, IV, also was formed when 7.4 g (0.02 mole) of III, m.p. $222-223^{\circ}$ C, in 10 ml of methanol was stirred for 48 hours with 1.4 ml (0.022 mole) of hydrazine hydrate at $35-40^{\circ}$ C. After removal of metallic mercury by filtration the system was vacuum-evaporated to leave a residue which was extracted with 100 ml of petroleum ether (b.p. $40-60^{\circ}$ C). The extracted residue (vacuum-dried) was washed onto a filter with cold 5% hydrochloric acid, then redried and crystallized from 95% ethanol (10 ml/g) to yield 1.2 g (17%), m.p. 185-186° C. Recrystallization from ethanol (7 ml/g) raised this melting point to 186.5-187° C and a mixture melting point with that obtained by hydroxymercuration was not lowered.

The petroleum ether extract was vacuum-evaporated to leave a residue which was crystallized from acetonitrile (4 ml/g), m.p. $61-62^{\circ}$ C, 1.8 g (64%) of crude $1,4-\uparrow\uparrow$ -methylenecyclohexane-2- \downarrow -carboxylic acid. Two recrystallizations from acetonitrile raised the melting point to $64.5-65.3^{\circ}$ C. A mixture melting point with an authentic sample (2) was not depressed.

$1,4-\uparrow\uparrow$ -Methylene- Δ^5 -cyclohexene-2- \downarrow -carboxylic Acid, I

A. By Deoxymercuration of III

To a suspension of 30.0 g (0.08 mole) of III, m.p. $222-223^{\circ}$ C, in 150 ml of methanol was added 20 ml (0.208 mole) of 36% hydrochloric acid, and the system was warmed to 50° C for 5 minutes, then maintained without heating and with occasional stirring for 15 minutes. The homogeneous system was maintained for 1 hour longer, then was cooled in ice and made alkaline with a slight excess of 10% aqueous sodium hydroxide (pH 7.3–10). After filtration of mercuric oxide the solution was vacuum-evaporated until methanol was gone, then was acidified to pH 3 with hydrochloric acid and was extracted with diethyl ether. Evaporation of the dried extract left a residue (9.45 g, 85%) which when crystallized from petroleum ether (b.p. 40–60° C) melted at 44–45° C, not depressed by admixture with 1,4- \uparrow -methylene- Δ ⁵-cyclohexene-2- \downarrow -carboxylic acid.

The deoxymercuration of III also may be effected completely in 5 minutes at 24° by treatment of 0.2 g of III with 0.5 ml of 36% hydrochloric acid. The same conversion to the endo unsaturated acid requires 15 minutes by use of 20.4% hydrochloric acid.

B. By Deoxymercuration of IV

When the methanolic deoxymercuration procedure described above was applied to IV a 3-hour reaction time was required to give an 80% yield of crude endo unsaturated acid, m.p. $36-38^{\circ}$ C. Crystallization from petroleum ether (b.p. $40-60^{\circ}$ C) raised this to $44.5-45.3^{\circ}$ C whence a mixture melting point with pure $1,4-\uparrow\uparrow$ -methylene- Δ^{5} -cyclohexene-2- \downarrow -carboxylic acid proved the identity.

When 0.1 g of IV was treated with 0.25 ml of 36% hydrochloric acid for 5 minutes at 24° C, then diluted with 0.25 ml of water, the filterable portion, washed with water and then with diethyl ether, weighed 0.05 g and melted at 185–186° C. A mixture melting point with IV was not depressed. When the initial hydrochloric acid concentration was 20.4% only 15% of IV was deoxymercurated in 15 minutes.

C. By Deoxymercuration of III plus IV

To an intimate mixture of 0.2 g of III and 0.10 g of IV was added 0.5 ml of 36% hydrochloric acid. After 5 minutes at 24° C and then dilution with 0.5 ml of water the filtered solid phase was shown to be 0.045 g

(45%) of IV of high purity (m.p. 185–186° C). A mixture melting point was not lowered. When 20.4% hydrochloric acid was used the recovery of IV only was 90%, m.p. 184–185° C.

5- \downarrow -Hydroxy-1,4- $\uparrow\uparrow$ -methylenecyclohexane-2- \downarrow -carboxylic Acid, γ -Lactone, V

A. From III

A clear solution of 7.4 g (0.02 mole) of 6- \downarrow -hydroxy-5- \downarrow -chloromercuri-1,4- $\uparrow\uparrow$ -methylenecyclohexane-2- \downarrow -carboxylic acid, γ -lactone, III, in 100 ml of 1% aqueous sodium hydroxide was cooled to -2° C and swirled while 2.6 g (0.022 mole) of sodium trimethoxyborohydride was added during 30 minutes. Then the black suspension was allowed to warm to 40° C and was filtered to remove 3.9 g (97%) of mercury.

The cold filtrate was carefully acidified with 5% aqueous sulphuric acid to pH 3 and then was extracted with diethyl ether. Evaporation of the dried extract left 2.15 g (76%), slightly sticky but melting at 146–149° C. After sublimation at 60–65° C at 0.7 mm and threefold crystallization from petroleum ether (b.p. 90–100° C) the melting point was raised to 155.5–156.5° C. A mixture melting point with an authentic specimen (6) was not lowered.

B. From IV

The identical procedure outlined above was applied to $6-\downarrow$ -hydroxy-5- \uparrow -chloromercuri-1,4- $\uparrow\uparrow$ -methylene-cyclohexane-2- \downarrow -carboxylic acid, γ -lactone, IV, with identical result.

Hydroxymercuration of 1,4- $\uparrow\uparrow$ -Methylene- Δ ⁵-cyclohexene-2- \uparrow -carboxylic Acid

To a stirred solution of 2.76 g (0.02 mole) of methylenecyclohexene-2- \uparrow -carboxylic acid in 75 ml of 1:1 2,5-dioxahexane-water mixture at 65–70° C was added during 1 hour a solution of 6.4 g (0.02 mole) of mercuric acetate in 50 ml of 98:2 water – acetic acid. After 2 days of subsequent stirring the system was filtered to remove 0.2 g of grey solid and then was made alkaline to pH 10. More grey solid (50 mg) was filtered off and the filtrate, after 2.1 g of sodium chloride was dissolved in it, was acidified by addition of gaseous carbon dioxide. After filtration this solution at pH 5–6 was vacuum-evaporated. The residue was Soxhlet-extracted with absolute alcohol, leaving a solid residue, A, and an extract, B.

Hydroxy-chloromercuri-1,4- \uparrow -methylenecyclohexane-2- \uparrow -carboxylic Acid, VIII

The solid residue, A, was washed with 0.5% hydrochloric acid, then with water, and was filtered to remove 1.2 g (15%) of crude chloromercurial m.p. 199–206° C. Two crystallizations by solution in 25 ml of 1:4 dioxane–ethanol followed by dilution with 15 ml of commercial hexane raised this melting point to 216–217° C. The mother liquors were combined with extract A. The infrared spectrum (potassium chloride pellets at 20,000 p.s.i., 24° C) of the mercurial, VIII, is expressed as wave numbers versus extinction: (3144) 8.21; (2920) 6.26; (2584) 4.37; (1681) 14.6; (1441) 4.81; (1418) 5.60; (1361) 11.3; (1333) 8.46; (1297) 5.48; (1267) 4.81; (1247) 2.25; (1233) 3.99; (1209) 2.92; (1159) 0.84; (1126) 2.48; (1110) 1.00; (1055) 3.91; (1033) 4.99; (1020) 4.42; (1007) 7.17; (967) 2.74; (939) 0.56; (912) 2.58; (883) 2.74; (869) 2.58; (835) 1.92; (777) 2.07; (769) 2.58; (759) 3.81; (723) 4.37; (651) 3.27. Anal. Calc. for C₈H₁₁O₈HgCl: C, 24.6; H, 2.81. Found: C, 24.9; H, 3.09. The extrapolated dielectric constant of the pelleted solid (8, 11) (Fig. 1) was found to be 2.347 and its density by flotation was 2.004, so distortion polarization is 60.5 cc by contrast to 53.9 cc calculated additively from Eisenlohr values.



FIG. 1. Extrapolation of apparent ϵ to zero thickness, VIII.

Hydroxy-chloromercuri-1,4- $\uparrow\uparrow$ -methylenecyclohexane-2- \uparrow -carboxylic Acid, IX

The acid and water washings, together with the crystallization mother liquors obtained in the preceding experiment, were combined with extract A above and the whole was vacuum-evaporated to dryness. The residue was eluted with absolute ethanol. The vacuum-evaporated eluate was washed onto a filter with 25 ml of 0.5% hydrocholoric acid; 5 g (64%) of crude chloromercurial, m.p. 159–170° C, was obtained. After two crystallizations from acetonitrile (30 ml/g) the product melted at 171–172° C, identical, by mixture melting point, with that obtained during the original separation of norbornenecarboxylic acids. The infrared spectrum (pellets as described above) expressed as (cm⁻¹) is: (3236) 9.67; (2924) 5.42; (1695) 15.6; (1445) 0.77; (1443) 0.74; (1364) 3.94; (1324) 2.40; (1292) 3.35; (1250) 3.14; (1235) 5.29; (1178) 7.49; (1139) 9.05; (1065) 5.42; (1031) 2.33; (1013) 6.34; (1003) 6.34; (947) 1.74; (911) 3.07; (887) 1.79; (823) 2.07. Anal. Calc. for C₈H₁₁-O₈H₂Gl: C, 24.6; H, 2.81. Found: C, 24.9; H, 3.20.

When the entire experiment was conducted without 2,5-dioxahexane for solubilization, the diastereomers

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m.p. 216° C and 172° C were obtained in yields of 8 and 22% respectively; much exo acid was recovered unchanged.

Deoxymercuration Rates of VIII and IX

Into 5 ml of 20% hydrochloric acid at 25° was stirred 0.1 g of finely powdered chloromercurial IX, m.p. 171–172°. After 15 minutes the system was diluted with 10 ml of water and filtered to remove 0.008 g (8%) of the original mercurial. When these conditions were reproduced upon 0.1 g of VIII 52% was recovered unchanged.

When 0.1 g each of VIII and IX were stirred into 10 ml of 20% hydrochloric acid for 15 minutes and then diluted with 20 ml of water the recovered mercurial (0.048 g, 48%) melted at 212–215° and was shown by mixture melting point with an authentic specimen, m.p. 214–216°, to be chiefly VIII.

Reduction of VIII and IX with Sodium Borohydride

A solution of 3.4 g (8.7×10^{-3} mole) of either VIII or IX in 25 ml of 5% aqueous sodium hydroxide was chilled to -5° , and 0.38 g (0.01 mole) of sodium borohydride was added portionwise during 10 minutes. After 1 hour the cooling bath was removed and the system at room temperature was just acidified with 2 N hydrochloric acid. The metallic mercury (1.64 g, 94%) was filtered off. The filtrate was five times extracted, with a total of 75 ml of diethyl ether, and this extract, dried by use of sodium sulphate, was distilled under 0.3 mm.

The product from IX boiled at 157–160°, 0.45 g (30%), m.p. 105–110°. Crystallization from benzene raised this melting point to 114–115°. A Nujol mull of this product, X, showed strong hydroxyl absorption at 3430 cm⁻¹ and carboxyl absorption at 1704 cm⁻¹. The hydroxyl absorption at 1010 cm⁻¹ appeared as a doublet. Anal. Calc. for $C_8H_{12}O_3$: C, 61.5; H, 7.75. Found: C, 61.3; H, 7.59.

The product from VIII boiled at 146–152°, 0.36 g (22%). It melted at 131–135° after crystallization from 2 ml benzene. Recrystallization from the same solvent raised this melting point to 134–136°. The spectrum from this product, XI, resembled that of X except that only a single peak was found at 1008 cm⁻¹. Anal. Calc. for $C_8H_{12}O_3$: C, 61.5; H, 7.75. Found: C, 61.5; H, 7.52.

Electrical Polarization Studies

The high value of distortion polarization (P_D) found for VIII by extrapolation of the dielectric constants of various thicknesses of compressed wafers (11) (Fig. 1) indicates that the calculation of electronic polarization from summation of bond or group refractions may introduce a minor error in the results of Table I. These summations have been used in every instance except for IX, where P_D for VIII was subtracted from the total polarization to arrive at the orientation polarization from which the moment is calculated. The error is slight and it applies also to the determination of dielectric constants for the dicarboxylic acid series (1).

Two grades of dioxane were used for determination (11) of total solute polarizations. Dioxane of $\epsilon = 2.2183$ and $\overline{V} = 0.96803$ was used for the values shown in Fig. 2 and of $\epsilon = 2.2276$ with $\overline{V} = 0.96775$ for the values shown in Fig. 3. Both figures show extrapolations to zero concentration of ϵ and \overline{V} for various strengths of solutions.



FIG. 2. Extrapolations of apparent ϵ and \overline{V} . A: 6- \downarrow -Hydroxy-5- \downarrow -chloromercuri-BCH-2- \downarrow -carboxylic acid, γ -lactone, III; B:6- \downarrow -hydroxy-5- \uparrow -chloromercuri-BCH-2- \downarrow -carboxylic acid, γ -lactone, IV; C:?-hydroxy-?-chloromercuri-BCH-2- \uparrow -carboxylic acid, IX.

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FIG. 3. Extrapolations of apparent ϵ and \overline{V} . E: 6- \downarrow -Hydroxy-BCH-2- \downarrow -carboxylic acid, γ -lactone, V; F: bicycloheptane-2- \downarrow -carboxylic acid; G: bicycloheptane-2- \uparrow -carboxylic acid.

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