THE MECHANISMS OF OXYMERCURATION[1]

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ABSTRACT

The oxymercuration of norbornenes has been found to be acid-catalyzed, and to give oxymercurials which have a higher dipole moment and greater stability toward deoxymercuration than do their diastereomers in which the configuration of the mercuri linkage has been inverted. Since these properties can be correlated with those of the oxymercurials from norbornenedicarboxylic acids (partly published heretofore and elaborated in the present report) the configurations of which are known, it follows that the configurations of the oxymercurials from norbornene are ↑↓ (*trans*). But these configurations must be opposite to those of the oxymercurials from cyclohexene, cyclopentene, α-terpineol, and the geoisomeric stilbenes, the formations of which are not acid-catalyzed and the dipole moments of which are lower than those of the diastereomers inverted with respect to the mercuri linkage. The configuration of these oxymercurials must be ↓↓ (*cis*) and the mechanism of their formation must be different from the acid-catalyzed oxymercuration of norbornene. The mechanism for *cis* (↓↓) addition has previously been suggested as non-ionic. Calculation of the electric moments of these ↓↓ diastereomers shows that hindrance to group rotation must prevail. It is reasonable to attribute the relative ease with which they may be deoxymercurated to this hindrance.

For some years there has been a difference of opinion in respect of the mechanism whereby the elements of hydroxy- or alkoxy-mercuric salts add to alkenes. This controversy is of interest beyond that of the oxymercurials because oxymercuration may provide an insight of alkene reactions not provided by less definitive reactions of these hydrocarbons. Thus it has been observed that oxymercuration is generally entirely stereospecific, with simple second-order kinetics in which a *cis*-geometric isomer is oxymercurated at a faster rate than is its *trans*-modification. However, none of these characteristics define the mechanism of reaction.

In 1935 the reaction was specified as an addition of molecular hydroxy- or alkoxymercuric acetate to the carbon–carbon double bond (1), and this belief that the added groups were in contiguous (so-called *cis*) configuration was reiterated in 1947 (2). Meanwhile, the alternative postulation has been made (3) that an ionized alkane–mercurinium salt is first formed from an ionizable mercuric salt and an alkene. The cation of this salt is subsequently attacked by a nucleophilic hydroxide or alkoxide ion, with inversion, to produce the oxymercurial in which the added groups are in the non-contiguous (so-called *trans*) relationship to one another. This mechanism is portrayed here for the oxymercuration of 1,4-methylene-Δ^2-cyclohexene (norbornene, I).

It might be predicted from this mechanism that the reaction would be favored by a system in which the ionization of mercuric salts would be enhanced. Moreover, the prevalence of the two possible products, 3-↓-methoxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric salt (IV) versus 3-↓-acetoxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric salt (III), ought to depend upon the relative activities of the anions $X^{\ominus}$ (usually acetate) and $OCH_3^{\ominus}$ in the system.

The oxymercuration of norbornene, I, has been found to conform with these predictions. A quantitative yield of III is formed rapidly when I is treated with mercuric acetate (X = OAc) in acetic acid. More specifically, a 0.34 molar solution of mercuric acetate in 2,5-dioxahexane converts 1 equivalent of norbornene into nearly pure 3-↓-acetoxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric salt (III, X = Cl after treatment with aqueous sodium chloride, m.p. 126–128°) in 98% yield during 30 minutes. Neither rate

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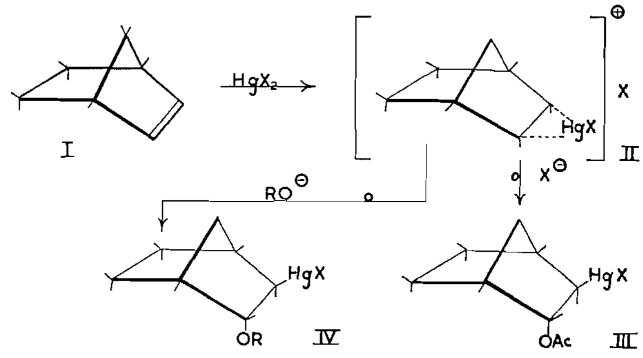


$$CH_3OH + X^{\ominus} \rightleftharpoons CH_3O^{\ominus} + HX$$

nor yield is diminished by inclusion of either 1 or 0.1 equivalent of boron fluoride etherate, although 0.1 equivalent of pyridine decreases the yield to 62% and 1 equivalent to 24% during 30 minutes. The effect of pyridine may be expected because of its tendency to coordinate with mercuric salts.

The configuration of this oxymercurial has been studied. The position of the acetoxy group in III (X = Cl) has been proved by saponification to be 3-↓-hydroxy-1,4-↑↑-methylene-2-↑-cyclohexylmercuric chloride (IV, R = H). This substance may be reduced by use of hydrazine hydrate in large excess to 3-↓-hydroxy-1,4-↑↑-methylenecyclohexane, identical with that obtained by Alder, Stein, and Rickert (4, 5) and configurationally established by Alder and Windemuth (6). The position of the chloromercuri group seems to be *trans* (↑) with respect to the acetoxy substituent according to the comparatively high dipole moment (3.6 Debye) which III (X = Cl) displays in dioxane. Therefore, the oxymercuration seems to have occurred via the alkane–mercurinium salt, II.

The same mode of reaction seems to occur when an equivalent of methanol is included with the mercuric acetate and norbornene in 2,5-dioxahexane but the product is IV (R = CH_3), as might be expected if methoxide ion were strongly nucleophilic in this medium. The configuration of 3-↓-methoxy-1,4-↑↑-methylene-2-↑-cyclohexylmercuric chloride (IV) corresponds with that of III because the 3-↓-hydroxy analogue to which III has been converted may be methylated in good yield (7) to the methoxy analogue, IV.

In protonic media the oxymercuration of norbornene is less simple. In water a mixture of III and IV (R = H, X = Cl after sodium chloride treatment) is obtained from which pure IV may be obtained by saponification. In methanolic solution, 0.00025 molar in I, and mercuric acetate a 97% yield of a mixture comprising 65% of IV (R = CH_3) and 35% of III is obtained. This behavior, not usual in the preparation of oxymercurials, would seem to be due to competition in nucleophilic attack of an intermediate like II by alkoxide and acetate ions. The following experiments substantiate this belief.

In Table I, items 1 to 4, is shown a series of experiments in which the molarity of norbornene and mercuric acetate in methanol has been lowered by dilution with this solvent. The products from these 90-minute experiments have been analyzed by melting point – composition diagram and by acetyl determinations.

It may be seen that upon increased dilution the yield is first increased and then essentially is constant. Of greater significance is the increasing amount of methoxymercurial (IV) instead of acetate (III) in the product. Item 11 shows that this tendency is independent of the absolute quantity of mercuric acetate in the system, although item 12, like

TABLE I

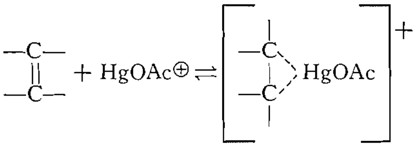
Oxymercuration of norbornene by mercuric acetate in methanol during 90 minutes followed by dilution into aqueous sodium chloride (X = Cl)

Item	Molarity of I and $Hg(OAc)_2$ in MeOH $\times 10^3$	Excess equiv. $Hg(OAc)_2$	Equiv. NaOAc	Equiv. HOAc	Total yield, %	% IV in total
1	0.5				86	61
2	0.25				97	66
3	0.1				93	73
4	0.07				95	86
5	0.25			1	85	80
6	0.25			5	69	73
7	0.25			20	69	67
8	0.25		1		73	21
9	0.25		2		60	15
10	0.25		10		81	10
11	0.04	9			99	90
12	0.12	3			90	60

item 1, shows that a high ratio of mercuric acetate to norbornene tends to decrease the formation of IV in favor of III. These behaviors might be expected if formation of methoxide ion were a consequence of equation [i] to which the reaction of equation [i] furnished little acetate because of limited dissociation.

Consideration of equations [i]–[vii] permits explanation of the results shown in Table I.

$$Hg(OAc)_2 \rightleftharpoons HgOAc^{\oplus} + OAc^{\ominus} \qquad [i]$$

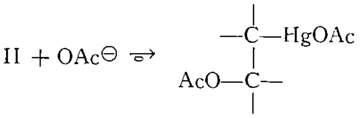


$$\text{I} + HgOAc^{\oplus} \rightleftharpoons \left[\text{C} \overset{\cdot}{\underset{\cdot}{\rangle}} HgOAc \right]^{+} \text{(II)} \qquad [ii]$$

I II

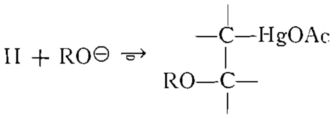
$$HOAc \rightleftharpoons H^{\oplus} + OAc^{\ominus} \qquad [iii]$$

$$ROH + OAc^{\ominus} \rightleftharpoons RO^{\ominus} + HOAc \qquad [iv]$$



$$\text{II} + OAc^{\ominus} \rightarrow \text{AcO—C—C—HgOAc} \qquad [v]$$

III



$$\text{II} + RO^{\ominus} \rightarrow \text{RO—C—C—HgOAc} \qquad [vi]$$

IV

$$Hg(OAc)_2 + ROH \rightleftharpoons RO\text{—}HgOAc + HOAc \qquad [vii]$$

$$HgO + 2HOAc \rightarrow Hg(OAc)_2 + H_2O \qquad [viii]$$

The reaction involving norbornene (I), mercuric acetate, and methanol may be adequately described by these equations. Dilution of the solution of reactants with methanol as indicated in items 1–4, Table I, would result in increased formation of methoxide ion and reduction of acetate ion by equation [iv]; thus favoring the formation of IV as described by equation [vi] at the expense of formation of III by equation [v]. Reduction of acetate ion would result in increased formation of the acetoxymercurinium ion (equation [i]). Thus increased dilution of the reactants with methanol would favor increased ionization of the mercuric acetate and would result in an increased yield of III plus IV in 90 minutes.

An equilibrium shift of the reaction described by equation [i] ought to be enhanced more by the ionization of acetic acid than by mercuric acetate. This expectation is realized in item 5 and to a certain extent in item 6, by comparison with item 2, but item 7 shows when addition of acetic acid reaches the 20-equivalent level the presence of acetate ion starts to favor the formation of III to the detriment of IV.

Inclusion of varying amounts of acetic acid (items 5–7, Table I) should reduce the over-all per cent yield in 90 minutes. The reason for this reduction is readily found by interpretation of equations [i]–[vii]. The increase in the ratio of III:IV produced by addition of acetic acid (and thus increased acetate ion) is explicable by consideration of the ratio, acetate: methoxide ion.

Inclusion of sodium acetate, a salt highly ionized in methanol compared with acetic acid, should further enhance the effect observed with added acetic acid. Addition of 10 equivalents of sodium acetate (item 10) increases the amount of the acetoxymercurial III to 90% of the total product.

According to these evidences of ionic participation it would follow that conditions in which basic mercuric salts would be prevalent ought to decrease the rate of reaction. This condition has been devised by inclusion of mercuric oxide into the methanolic system 0.25 molar in norbornene and mercuric acetate. In this experiment, the reaction shown in equation [viii] would be operative together with the reactions described by equations [i]–[vii]. After 4 hours the total yield is only 70% but the acetic acid liberated from this amount of oxymercuration has by this time dissolved the suspended mercuric oxide. Subsequently the yield rises to 90%. Of interest is the observation that the 90% yield contains at least 10% more of the methoxymercurial than is obtained from the reaction system in which no mercuric oxide is present.

This evidence that methoxymercuration of norbornene is retarded in a basic or neutral environment would indicate that this reaction would be favored in acidic media. The data of Table II substantiate this prediction.

The addition of only 0.02 equivalent of sulphuric acid increases the amount of methoxymercurial, IV, relative to the acetate, III, from 67 to 85%. While the addition of larger amounts of sulphuric acid tends slightly to decrease the total yield (deoxymercuration), the percentage of IV in this total actually is increased. It would appear that the bisulphate ion, itself not sufficiently nucleophilic to undergo neutralizing addition to an alkane–mercurinium salt, removes acetate ion from the system according to equation [ix]. The behavior of methoxyfluoboric acid

$$\mathrm{Hg(OAc)_2} + \mathrm{H}^{\oplus} + \mathrm{HSO_4}^{\ominus} \leftrightarrows \mathrm{HgOAc}^{\oplus} + \mathrm{HSO_4}^{\ominus} + \mathrm{HOAc} \qquad [ix]$$

and *p*-toluenesulphonic acid probably are similar. In this connection it may be observed that hydrochloric acid does not increase the yield of IV, undoubtedly because it is converted to mercuric chloride which is largely unionized.

It may be seen from the table that odd electron donors such as benzoquinone, hydroquinone, and *tert*-butylhydroperoxide are entirely ineffective. To be sure stannous chloride and ferrous sulphate are both effective for augmentation of IV over the acetate, III, but they may be functioning in formation of complex anions. The augmentation by the ferrous salt is of especial interest if the present findings are contrasted to an earlier report of the preparation of 3-methoxymethylenecyclohexylmercuric chloride (8) in which

TABLE II

The effect of catalysts on oxymercuration with norbornene and mercuric acetate 0.25 molar in methanol during 90 minutes

			% of IV in product	
Catalyst	Equiv. of catalyst	Total yield, %	From acetyl content	By thermal analysis
Sulphuric acid	0.02	92		85
	0.10	85	90	89
	0.50	85		93
	1.00	85		93
p-Toluenesulphonic acid hydrate	0.10	90	86	83
	2.5	95		95
Ferrous sulphate	0.05	75	80	79
Boron fluoride etherate	0.10	95	90	89
Stannous chloride	0.10	65	79	81
Hydroquinone	0.10	93		69
Benzoquinone	0.10	95		68
Hydrochloric acid	0.10	83		68
tert-Butylhydroperoxide	0.10	93		67
None		97		67
Pyridine	0.10	95	58	55
	1.00	89	37	30
Trimethylamine	0.10	90	24	21

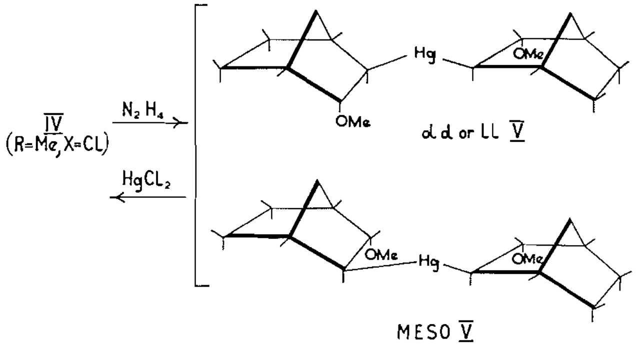
a good yield in high purity seemingly was obtained with a system comprised only of norbornene, mercuric acetate, and methanol. In view of our findings with this system, we presume that a contaminant such as ferrous salt must have been present in Rowland's system since otherwise he could not have obtained the high yield of methoxymercurial which he reported. Rather he should have obtained a mixture of III and IV.

In addition to the substances which accelerate the methoxymercuration over the formation of 3-↓-acetoxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric salt (III), it may be seen from Table II that tertiary amines like pyridine and trimethylamine strongly retard methoxymercuration in favor of the formation of III. This must be due to the augmentation of acetate ion from the acetic acid formed in the system. Of course these nitrogen-containing electron-donors have been known previously to retard methoxymercuration, and earlier in this report it was shown that pyridine retarded the formation of III in 2,5-dioxahexane. Probably these latter effects are inconsequential to the argument of Table II. It may be seen that the presence of the amines did not appreciably diminish the total yield in methanol. Actually, the effect of either acids or bases on the rate of norbornene oxymercuration has not been evaluated in the present study because the reaction, even without addends, is very fast. Although 90 minutes has been allowed in these studies in order that all reactions would be standardized with respect to time, it is known that the 0.25 molar reaction in methanol at 20° C is complete within 45 seconds.

One may ask how this evidence for an ionic mechanism of oxymercuration may be correlated with previous experience of the general reaction. For example, it has been shown (9) that acetic acid retards one oxymercuration while the removal of acetic acid by evaporation from another, typical, reaction increases the rate (10). Moreover the evidence for ↑↑ (*cis*) addition is strong in respect of general oxymercuration (11), except for an X-ray diffraction study (12) which may be questioned in view of recent opinions about the flexibility of the cyclohexane ring. In view of these experiences the present results might seem to be anomalous.

An explanation has been sought, and found, in the chemical and physical properties of the norbornene methoxymercurials. First, the stability of the product designated as 3-↓-methoxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric chloride (IV, R = Me, X = Cl) is unusually high. This stability is apparent also in the products obtained when IV is treated with excess hydrazine hydrate. For the first time this reaction has yielded methoxyalkyl bis-mercurials; both diastereomers have been obtained as solids which were separable by fractional crystallization. Either diastereomer can be reconverted to the original chloromercurial, IV, so that the reconversion of the bis-mercurial is stereospecific. We consider the higher melting (108°) bis-mercurial to be the meso isomer, V; also it has the higher dipole moment (2.17 D in benzene).

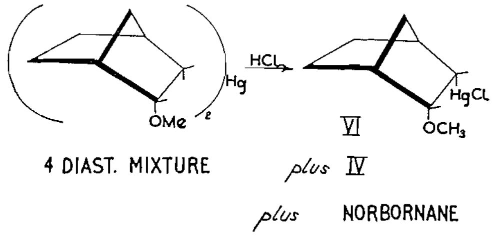
A second evidence of the stability of IV has been observed by the diastereomeric equilibration of IV (↓↑) with its isomer (↓↓, VI) with a small amount of hydrazine hydrate. This reaction has been shown (13) to give diastereomeric mixtures of 2-oxycyclohexyl and 2-oxycyclopentyl mercurials. The more stable diastereomer in the mixture may be isolated by treatment with methanolic hydrogen chloride which deoxymercurates the other diastereomer. The recovered diastereomer, which has been designated as β, has always heretofore been that one *not* obtained by oxymercuration of the alkene.



In contrast, the diastereomer recovered by partial deoxymercuration of the mixture of IV and VI is IV, the product of oxymercuration, in good yield. In order to isolate VI (at best, in small amount) an arduous fractional crystallization of the IV–VI mixture is required. This separation may be facilitated slightly by first converting the IV–VI mixture into a bis-mercurial mixture containing all four diastereomers, of which V represents a pair. This is accomplished by treatment of the IV–VI mixture with excess of hydrazine hydrate. When the four-diastereomer mixture is treated cautiously with less than the stoichiometric amount of methanolic hydrogen chloride for the reaction, the amount of VI in the mixture of IV and VI has been enhanced. Probably steric effects have altered the relative rates of diastereomeric scission.

The properties of VI do not resemble those of the previously known cyclic β-chloromercurials. It has been pointed out above that VI is more easily deoxymercurated than is IV, and this contrast to other cyclic α=β pairs is confirmed by the observation that the dipole moment of VI is found to be lower than that of IV. It would seem from these properties that the configurations of the norbornene oxymercurials are opposite to those of other oxymercurials such as are prepared from terpineol (14), cyclopentene (13), and cyclohexene (13, 15).

According to this definition of the configurations those assigned by Winstein, Traylor, and Garner (15) must be incorrect.

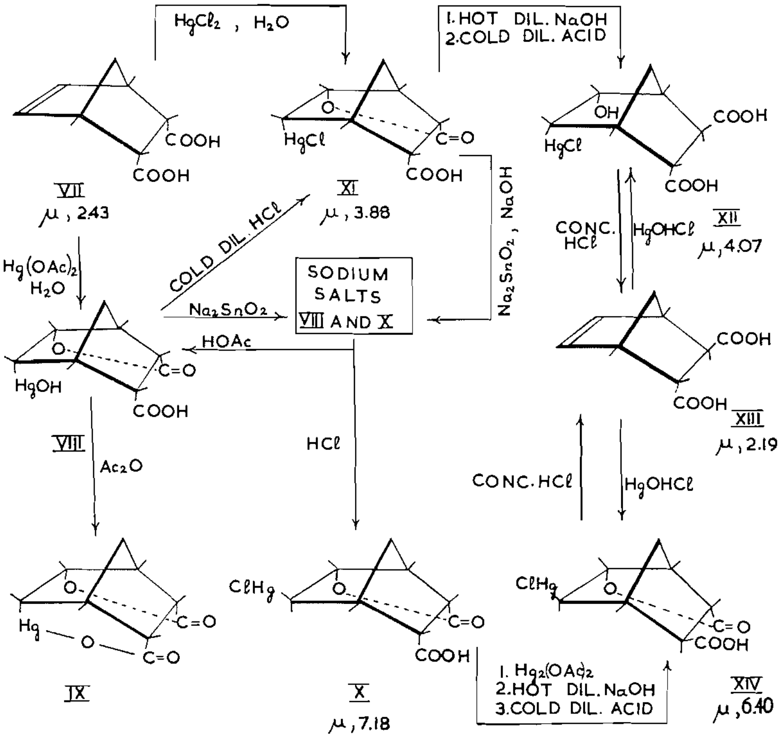


In contrast to the oxymercurations of cyclopentene and cyclohexene it may be said that the oxymercuration of norbornene is abnormal. This unusual behavior may not be unexpected in view of the dipole moments observed (Table III) for norbornane and norbornene, which would indicate a displacement of the electronic fields in these substances. Moreover, it has been shown previously (16, 17) that bromination of the norbornene-2,3-dicarboxylic acids does not follow the common ↑↓ addition of bromine to the double bond. During the remainder of this report it will be shown that some of these dicarboxylic acids also are abnormal in respect of oxymercuration.

During our previous work (11) with 1,4-↑↑-methylene-Δ^5-cyclohexene-2,3-↓↓-dicarboxylic acid (endo-norbornene-2,3-dicarboxylic acid, VII) we did not discern any abnormality when we established the *cis* (↓↓) configuration for the product (VIII) obtained by treatment of VII with aqueous mercuric acetate. Although the compound shown graphically as VIII could, alternatively, be 5-↓-hydroxy-anhydro-[6-↓-hydroxymercuri-2-↓-carboxy]-1,4-↑↑-methylenecyclohexane-3-↓-carboxylic acid, the choice of which transannular bridge is open is configurationally unimportant. Either form would be expected to undergo dehydration upon treatment with acetic anhydride to give 5-↓-hydroxy-anhydro-[6-hydroxymercuri-2-↓-carboxy]-1,4-↑↑-methylenecyclohexane-3-↓-carboxylic acid, γ-lactone (IX). The configuration of IX (and therefore of VIII) must be ↓↓ in respect of the oxy- and mercuri-linkages because its molecular weight has been determined cryoscopically as 381. The calculated molecular weight of IX is 382, so a polyester structure is not involved. The configuration of VIII and IX must therefore be ↓↓ as well.

It may be expected that the chloromercurial XI derived from VIII by acidification with hydrochloric acid also will have the ↓↓ configuration. But XI may be obtained directly by treatment of the unsaturated acid, VII, with mercuric chloride in water. This observation by Mr. J. H. Robson marks the first instance of oxymercuration in which participation of a basic mercuric salt cannot be postulated. Indeed, the near-quantitative yield is only lowered by 15% when 2 equivalents of hydrogen chloride are included with the mercuric chloride, although the otherwise very rapid reaction is retarded by this extra acid. The behavior is strongly suggestive of an ionic reaction which will be discussed later in this report.

When either VIII or IX is treated with aqueous sodium stannite the expected precipitation of metallic mercury occurs, and this presumably homopolar reaction (18) yields a diastereomeric mixture. Careful acidification with acetic acid precipitates VIII, perhaps in the anhydromercurial form mentioned above. After removal of VIII the filtrate may be acidified further by use of hydrochloric acid to yield the diastereomeric 5-↓-hydroxy-6-↑-chloromercuri-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic acid, γ-lactone (X). This compound may be deoxymercurated (by treatment with concentrated hydrochloric acid) to the same 5-↓-hydroxy-1,4-↑↑-methylenecyclohexane-2,3-↓↓-di-



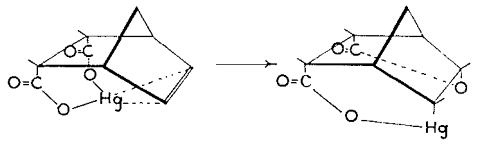
carboxylic acid, γ-lactone, obtained (more easily) by similar deoxymercuration of XI. The latter also yields, with sodium stannite, a mixture from which X may be isolated but the yield is lower, probably because of the presence of chloride ion.

When XI is boiled with aqueous sodium hydroxide it is converted (evidently via lactone hydrolysis) by prototropic rearrangement into 5-↓-hydroxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2-↓-3-↑-dicarboxylic acid (XII). The alteration in the rearranged substance is proved by deoxymercuration to 1,4-↑↑-methylene-Δ^5-cyclohexene-2-↓-3-↑-dicarboxylic acid by means of hydrochloric acid. Further proof is obtained when XII is treated with sodium amalgam, which effects replacement of chloromercuri by hydrogen. The product (which shows no tendency toward spontaneous lactonization) evidently is 5-↓-hydroxy-1,4-↑↑-methylenecyclohexane-2-↓-3-↑-dicarboxylic acid.

The prototropic rearrangement of XI→ XII is replicated by the conversion X → XIV, although the absence of chloride ion is essential to the latter conversion. The chloride was precipitated as calomel. The 2-carboxyl group seems to be rearranged, since XIV is the lactone of what must be 5-↓-hydroxy-6-↑-chloromercuri-1,4-↑↑-methylenecyclohexane-2-↑-3-↓-dicarboxylic acid. Confirmation of this structure assignment follows deoxymercuration of XIV with concentrated hydrochloric acid, which yields 1,4-↑↑-methylene-Δ^5-cyclohexene-2,3-↓↑-dicarboxylic acid (XIII). Moreover, replacement of the chloromercuri group (with sodium amalgam) by hydrogen leads to the known 5-↓-hydroxy-1,4-↑↑-methylenecyclohexane-2-↑-3-↓-dicarboxylic acid, γ-lactone (19).

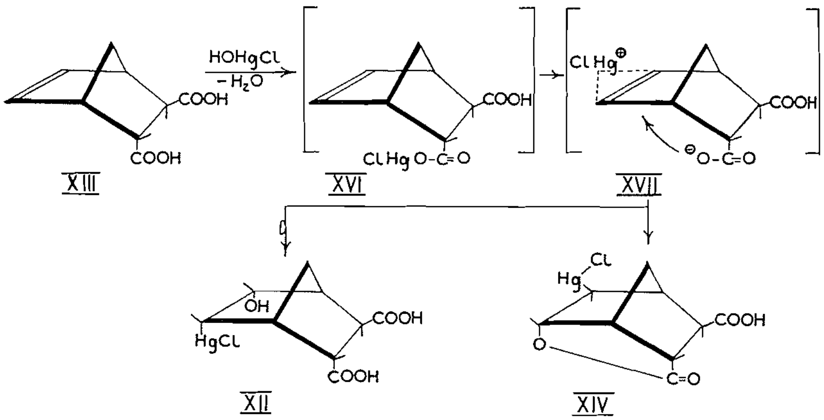
The oxymercurial from norbornene has been assigned the ↑↓ configuration and that from 1,4-↑↑-methylene-Δ^5-cyclohexene-2,3-↓↓-dicarboxylic acid (VII) the ↓↓ configuration (XI), yet both reactions seem to proceed by the same (ionic) mechanism. It might then be expected that a reaction would exist in which both ↓↓ and ↑↓ configurations would appear in the product. This expectation is realized in the treatment of 1,4-↑↑-methylene-Δ^5-cyclohexene-2,3-↑↓-dicarboxylic acid (XIII) with basic mercuric chloride in water, since both XII and XIV are obtained as products with the former predominating.

From these examples, it seems reasonable to assume that the norbornenes are oxymercurated uniquely via a π complex with mercuric salts which once was specified for alkenes in terms of an alkene–mercurinium ion (3). The favored neutralization of such an intermediate seems to occur from that region of the norbornane cage farthest from the methylene bridge. The mercuri group will then be situated in that region of the cage where the methylene bridge is predominant, unless it is attracted by an anionic group such as carboxyl in an available (↓) position. The simplest instance where both neutralizing anion and mercuri-attracting anion are two ↓↓ carboxyl groups is exemplified by the π-co-ordinated mercuric salt, XV, which is transformed to IX.



XV IX

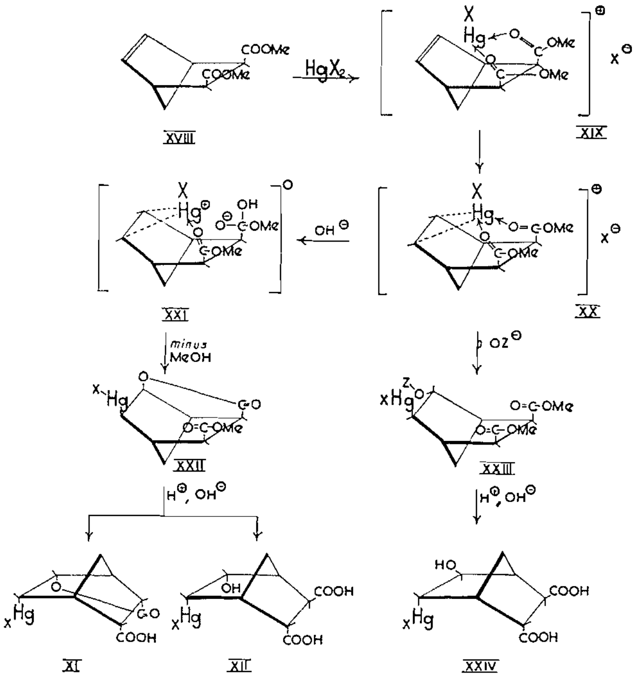
When only one ↓ carboxyl group is available, as in 1,4-↑↑-methylene-Δ^5-cyclohexene-2-↓-3-↑-dicarboxylic acid (XIII), it seems to play either of the two roles alternatively. Thus it may neutralize the cation XVII formed via the intermediate XVI to yield XIV, or it may attract the mercuri group while hydroxyl ion is the neutralizing species, in which case XII is formed. One might expect in these circumstances that some of the 5-↑-OH diastereomer would be formed despite a preferential anionic approach to the cage. We have not found this diastereomer, but we cannot affirm its absence in view of the difficulties of separation. We shall now present evidence that such anionic neutralization does occur.



This evidence is afforded by oxymercuration of dimethyl 1,4-↑↑-methylene-Δ^5-cyclohexene-2,3-↓↓-dicarboxylate (XVIII). Previously, the hydroxymercuration of this substance was reported (11) and the product was specified as 5-↓-hydroxy-6-↓-chloromercuri-2-↓-carbomethoxy-1,4-↑↑-methylenecyclohexane-3-↓-carboxylic acid, γ-lactone (XXII). It is now known that XXII from this reaction is contaminated with 5-↑-hydroxy-6-↓-

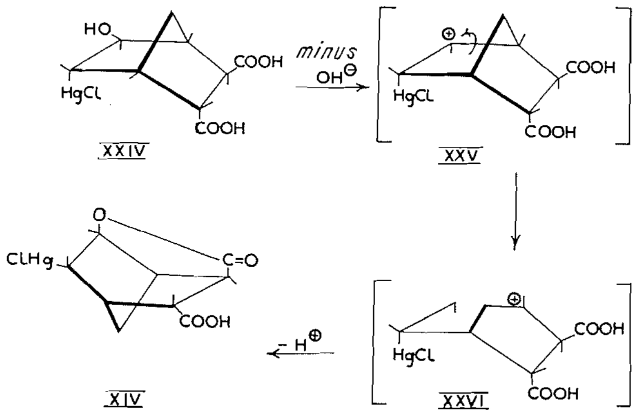
chloromercuri-2-↓-carbomethoxy-1,4-↑↑-methylenecyclohexane-3-↓-carboxylic acid, perhaps as its methyl ester, XXIII, though neither has been isolated. However, the presence of this mono- or di-ester impurity is shown by saponification of the entire product. The main product of this saponification is 5-↓-hydroxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic acid, γ-lactone (XI), as well as some of the 2-↓-3-↑-dicarboxylic acid (XII) arising by prototropic rearrangement of XI. The remainder is isolated as 5-↑-hydroxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2-↓-3-↑-dicarboxylic acid (XXIV), the chemistry of which is discussed below. Thus the dimethyl ester of VII is shown to oxymercurate both ↓↓ and ↓↑, the former being predominant.

When dimethyl 1,4-↑↑-methylene-Δ^5-cyclohexene-2,3-↓↓-dicarboxylate (XVIII) is treated with mercuric acetate in acetic acid, the reaction is very rapid. The main product, almost pure, is dimethyl 5-↑-acetoxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylate (XXIII, Z = CH_3CO) plus a small quantity of 5-↓-hydroxy-6-↓-chloromercuri-2-↓-carbomethoxy-1,4-↑↑-methylenecyclohexane-3-↓-carboxylic acid, γ-lactone (XXII, X = Cl). When XXIII (Z = CH_3CO) is hydrolyzed, a prototropic rearrangement of one carboxyl group occurs to yield XXIV. This shift is indicated because deoxymercuration of XXIV with hydrochloric acid yields 1,4-↑↑-methylene-Δ^5-cyclohexene-2-↓-3-↑-dicarboxylic acid (XIII). However, XXII (X = Cl), which may be prepared in excellent yield by mercuration of XVIII with an aqueous solution of mercuric acetate, and XXIII (Z = Me, X = Cl) prepared by methoxymercuration of XVIII, both deoxymercurate with hydrochloric acid to yield 5-↓-hydroxy-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic acid, γ-lactone. Of course, this does not indicate which carboxyl group in XXIII has diastereomerically shifted. Indeed, XXIV could be either 5-↑-hydroxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2-↓-3-↑- or 2-↑-3-↓-dicarboxylic acid, but a pyrolytic reaction seems to supply this information.



The 5-↑-hydroxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2-↓-3-↑-dicarboxylic acid (XXIV) exists in two forms which evidently are polymorphs since the distortion polarizations and the infrared spectra (900–300 cm^{-1}) are practically identical although the melting points and X-ray diffraction patterns are different. The lower melting of these polymorphs tends slowly to resolidify slightly above its melting point of 194°. If it is maintained at 194–200° for 15 minutes the recognizable product is 5-↓-hydroxy-6-↑-chloromercuri-1,4-↑↑-methylenecyclohexane-2-↑-3-↓-dicarboxylic acid, γ-lactone (XIV). This inversion of the methylene bridge seems to be characteristic of the configuration of XXIV (since XII did not rearrange in this manner) and probably is a consequence of the 5-↑-hydroxy configuration. The rearrangement may be described in terms of the intermediates XXV and XXVI, and is typical of dehydration which otherwise would establish a bridgehead unsaturation.

In order to eliminate the possibility that the oxymercuration position assignments were incorrect, and that XXIV and XII differed only in the configuration of the chloromercuri group, the acid XXIV has been treated with sodium amalgam. The product has been designated as 5-↑-hydroxy-1,4-↑↑-methylenecyclohexane-2-↓-3-↑-dicarboxylic acid; certainly it is not identical with the acid of like composition which has been obtained by reduction of XII. It would seem that XXIV and XII differ in the configuration of the hydroxyl group.



The configurations of the oxymercurials derived from dimethyl 1,4-↑↑-methylene-Δ^5-cyclohexene-2,3-↓↓-dicarboxylate seem to be established and the mode of their formations may be suggested. The mechanism may be described essentially as was that of the corresponding acid. If the ester (XVIII) co-ordinates with mercuric acetate (X = OAc) a near-ionic form, XIX, may occur. Within the electropositive portion further co-ordination with the π bond (XX) will be a prelude to further reaction. If the reaction occurs in water, hydroxyl ion may be expected to perform the first step of an ester hydrolysis, i.e. to add to the carbomethoxyl group and form the externally neutral dipole, XXI. This internal mercurinium salt, by loss of methanol, would then culminate in the principal product, XXII. If some hydroxyl ion (or the ever-present acetate ion X) were to attack rearward of the mercurinium linkage (OH or OAc = OZ) then the product of inversion (XXIII) is expected and, in small amount, is obtained. In absence of the hydrolytic reaction, that is, when the reaction medium is acetic acid, XXIII, the product of inversion, is obtained in 93% yield, and XXII in small amount (0.5%). This attack by acetate from the region of the cage where the methylene bridge predominates is contrary to that observed with norbornene. This opposite behavior is attributed in the present mechanism to the complexity of the ion, XX.

In connection with the ionic mechanism which has been postulated for the norbornenedicarboxylic acids and their derivatives it may be recalled that inclusion of boron fluoride etherate during the oxymercuration of norbornene largely excluded the acetoxy derivative, III, in favor of the methoxy derivative, IV (R = Me). This behavior is expected when acetate and methoxide ions are competing in an ionic process because of the preferential stabilization of methoxide ion by the Lewis acid, BF_3. It is of interest that the oxymercuration of the ester, XVIII, in methanol leads to XXIII in which Z is almost entirely aceto. However, a mixture is formed in which Z is partly methyl when boron fluoride is included with the methanol. Since the measured dipole moment of this methoxy derivative is of the same magnitude as that of XXIII (Z = CH_3CO), we presume that the configuration is identical. The mechanism of reaction thus seems to be the same as that postulated for oxymercuration of norbornene.

It will be noted in the preceding paragraph that configurational identity has been claimed on the basis of dipole moments. Also configurational relationships must be established between the mercurials from norbornenedicarboxylic acids (the configuration of which has been established by definitive physical and chemical criteria) and the mercurials from norbornene. Therefore the basis for the relationship according to the moment values of Table III must be established.

It must be understood that the moment values per se do not establish configurations but only relate known to unknown configurations. Moreover the moment values must only be considered of qualitative significance. Of course the actual values, all determined at 20° in dioxane (the only non-polar solvent in which all the mercurials are soluble), are reliable within 0.1 D. However, the vectorial assignments and the group moments must be chosen somewhat arbitrarily; indeed another set might have been chosen which would designate configurations opposite to those specified in this report. Nevertheless, like much physical interpretation based on factual logic and non-factual assumptions, the moment calculations are at least self-consistent. As such they suffice to relate the configurations assigned in this report.

Among the group moment assignments which must be made for the calculation is that of the chloromercuri group. A linear (20) and later an angular (21, 22) (+)C—Hg—Cl(−) has been proposed. The angularity must be revised anew in view of evidence (23) that the C—Hg moment is not negligible. Indeed, the measured polarizations of mercuracyclohexane and mercuracycloheptane (0.86 and 0.90 D respectively) show that the bond moment of C—Hg is 1.31 D, negative with respect to carbon, if the C—Hg—C angle is 140°. Then despite uncertainty of mercurial bond angles (23) one may assign to a typical mercurial, *n*-propylmercuric chloride (3.70 D), a C—Hg—Cl bond angle of about 80° if the Hg—Cl moment is 3.2 D. The latter value has been chosen in consideration of the increasing dipole moment of alkylmercuric halides with ascent of the homologous series (23). Essentially these assignments designate mercury as the positive end of the angular alkanemercuric chloride dipole.

A structural assignment must also be made for the gamma–lactone linkage. This assignment has not been made previously, perhaps because the reported values, 3.8 (24) to 4.1 D (25), for γ-butyrolactone are abnormally high by contrast with non-cyclic

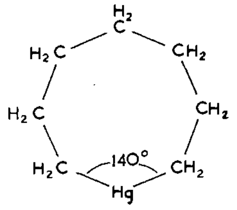
TABLE III

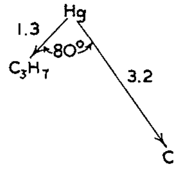
Electrical polarizations (cc) in dioxane at 20° C, moment in Debye units

	$\Delta\epsilon/\Delta\omega$	$\Delta\bar{V}/\Delta\omega$	P_T	P_{e+a} pellet	R_D calc.	μ
5-↓-Hydroxy-2-carbomethoxy-1,4-↑↑-methylenecyclohexane-3-↓-carboxylic acid, γ-lactone	15.53	0.165	542.9		45.1	4.86
1,4-↑↑-Methylene-Δ^5-cyclohexene-2,3-↓↑-dicarboxylic acid (XIII)	3.50	0.220	143.4		42.0	2.19
Same, except-2,3-↓↓-dicarboxylic acid (VII)	4.35	0.295	164.3		42.0	2.42
1,4-↑↑-Methylenecyclohexane-2,3-↓↓-dicarboxylic acid	5.50	0.230	204.8		42.4	2.78
1,4-↑↑-Methylenecyclohexane-2,3-↓↑-dicarboxylic acid	4.40	0.210	172.7		42.4	2.49
5-↓-Hydroxy-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic acid, γ-lactone	16.70	0.265	535.1		40.4	4.85
5-↓-Hydroxy-1,4-↑↑-methylenecyclohexane-2-↑-3-↓-dicarboxylic acid, γ-lactone	18.30	0.275	578.8		40.4	5.06
Dimethyl 5-↑-acetoxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylate (XXIII, Z = CH_3CO, X = Cl)	6.30	0.545	579.5		78.9	4.87
Norcamphane (norbornane)	0.09	0.210	34.11		30.1	0.43
Norbornene (I)	0.28	0.185	35.6		29.7	0.53
5-↑-Methoxy-1,4-↑↑-methylenecyclohexane-2,3-↑↑-dicarboxylic acid	6.00	0.295	249.9		47.6	3.10
5-↑-Hydroxy-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic acid	7.25	0.612	557.5	88.9	60.2	4.73
dd,ll-2,2′-↑↑-Mercuri-bis-3-↓-methoxy-1,4-↑↑-methylenecyclohexane, m.p. 68° (V, *dd,ll*)	1.0417	−0.36364	156.8	81.1	81.8	1.93
dl,ld of same, m.p. 108° (V, *dl,ld*)	1.250	−0.3333	176.2	81.4	81.8	2.17
3-↓-Methoxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric chloride (IV, R = Me, X = Cl)	6.250	−0.4500	427.5		52.4	4.22
3-↓-Methoxy-1,4-↑↑-methylenecyclohexyl-2-↓-mercuric chloride (VI)	2.857	−0.555	214.2		52.4	2.77
3-↓-Acetoxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric chloride (III)	4.40	0.505	329.8		57.1	3.60
5-↓-Hydroxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2-↓-3-↑-dicarboxylic acid (XII)	5.33	0.605	405.6		56.4	4.07
5-↓-Hydroxy-6-↑-chloromercuri-1,4-↑↑-methylenecyclohexane-2-↑-3-↓-dicarboxylic acid, γ-lactone (XIV)	9.90	0.610	716.1		56.4	6.40
5-↓-Hydroxy-6-↑-chloromercuri-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic acid, γ-lactone (X)	16.10	0.585	1143.4		56.4	7.18
Same, except -6-↓-chloromercuri- (XI)	4.85	0.600	373.0		56.4	3.88
5-↓-Hydroxy-6-↓-chloromercuri-2-↓-carbomethoxy-1,4-↑↑-cyclohexane-3-↓-carboxylic acid, γ-lactone (XXII)	4.50	0.545	366.6		61.1	3.81
Dimethyl 5-↑-methoxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylate (XXIII, Z = Me, X = Cl)	5.80	0.537	508.2		74.2	4.54

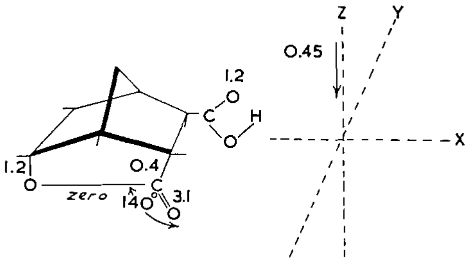
little-constrained esters. It seems reasonable to explain this high value as an alteration of bond moments in the —C—O—(C=O)—C linkage from [0.7, 0.7, 2.3, 0.4] to [0.8, 0.5, 2.8, 0.4], after which the moment for γ-butyrolactone is calculated as 4.0 D.

However, the moments of the 5-↓-hydroxy-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic acid, γ-lactone (μ = 4.85 D), and the 2,3-↑↓-diastereomer (μ = 5.06 D) markedly exceed that of γ-butyrolactone. Part of this abnormality may be ascribed to the norbornane ring since a moment of 0.43 D has been observed (Table III) for this hydro-





carbon. The carboxyl group will also contribute, but neither contribution suffices to explain the high moment which has been observed, especially for the 2,3-↑↓-diastereomer. However, it is probable that the additional constraint imposed by the norbornane cage accentuates the alteration in bond moment which has been suggested for γ-butyrolactone.



XXVII

These considerations have suggested the model XXVII in which the alcohol bond is extended to 1.2 D and the carbonyl bond is extended to 3.1 D, while the ester bond is decreased to zero. This condition represents a resonance hybridization of the O—C=O linkage. Moreover the constraint imposed by non-planarity of the γ-lactone ring has distorted the cyclohexane ring so that the ↓ linkages are inclined 18° toward the center of the cage, thus forcing the equatorial ↑ linkage into a plane containing atom 2, 3, 5, and 6. These linkages are assumed to be spread 30° outward from the X-axis.

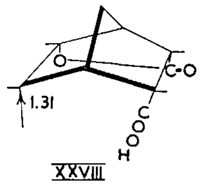
The moment of the free carboxyl group has been estimated as 1.2 D by calculation from the observed moments of 1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic acid (μ = 2.78 D) and 1,4-↑↑-methylenecyclohexane-2,3-↑↓-dicarboxylic acid (μ = 2.49 D) after subtraction of the norbornane cage moment (0.45 D). In order to simplify subsequent calculations the moment of the carboxyl groups (either ↑ or ↓) has been assumed to be symmetrical about the C—COOH bond. That is to say that the hydroxyl group in the carboxyl is in *cis* relationship to the carbonyl group.

In these circumstances the moment summation with respect to the co-ordinate axes is found to be 4.86 D for 5-↓-hydroxy-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic acid, γ-lactone, and 5.04 D for the 2,3-↑↓-diastereomer. If the C—Hg group moment assigned previously (1.31 D, C ← Hg) is added to each of these γ-lactones in the appropriate sense the following R—Hg moments arise from the calculation.

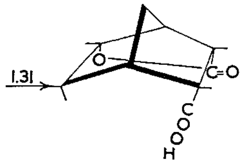
Calculation of the moment of 5-↓-hydroxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic acid, γ-lactone, from XXVIII may be made as follows:

$$\mu = [(3.79)^2+(3.22)^2-2(3.79)(3.22)\cos 41^\circ \cos 13^\circ \sin 10^\circ]^{\frac{1}{2}} = 4.6\ \text{D}.$$

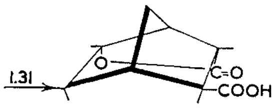
It is not surprising that this value, based on harmonic rotation at a rate exceeding 500 kc/second, is appreciably higher than the observed moment (3.88 D) since free rotation



XXVIII



XXIX



XXX

$\mu_{R\text{-}Hg} = 3.79$ D
where $\tan \mu_Y/\mu_Z = \tan 11°$
and $\tan \mu_X/\mu_Z = \tan 43°$

$\mu_{R\text{-}Hg} = 5.87$ D
where $\tan \mu_Y/\mu_X = \tan 23°$
and $\tan \mu_Z/\mu_X = \tan 43°$

$\mu_{R\text{-}Hg} = 6.31$ D
where $\tan \mu_Y/\mu_X = \tan 18°$
and $\tan \mu_Z/\mu_X = \tan 27°$

would be most improbable. Calculation at position 6 for the quadrant directions of Hg → Cl shows that when this vector points toward the 2-position the moment would be 6.2 D; away from position 2, 2.3 D; toward position 5, 5.0 D; and away from position 5, 4.3 D. Therefore the observed moment is about what would be expected if rotation were hindered within the realm of the norbornane cage, thus minimizing the 6.2 D and the 5.0 D conformations.

The moment calculation from XXIX for 5-↓-hydroxy-6-↑-chloromercuri-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic acid, γ-lactone (X), assuming free rotation, is 7.0 D. While this is lower than the observed moment (7.18 D) the slight discrepancy is not unexpected in view of possible hindrance when Hg → Cl is directed toward C_5. This conformation detracts slightly from the total because of the angle of 120° which the Hg—C bond makes with the C_5—C_6 bond. Consequently, the observed moment may be expected to be slightly higher than that calculated for harmonic free rotation.

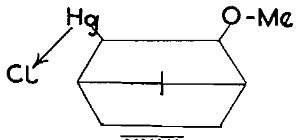
However, a greater discrepancy exists between observed moment (6.4 D) and that calculated (7.50 D) from the partial structure, XXX, for 5-↓-hydroxy-6-↑-chloromercuri-1,4-↑↑-methylenecyclohexane-2-↑-3-↓-dicarboxylic acid, γ-lactone (XIV). Several explanations are possible to account for this discrepancy. First, the assumption that the carboxyl group is bound so that its group moment is linear may apply to the ↓ position where it is "bound" by the lactone resonance but not to the ↑ (actually equatorial) position. Thus it may contribute, together with the chloromercuri group, three rotators in the structure. The equation for a single rotator would then not apply. More likely is the possibility that this heavy molecule exists as a carboxylic acid dimer which is stable even in very dilute solution because of the non-hindered equatorial carboxyl group. This hydrogen-bridging would effectively lower the moment. Some evidence for this bridging is found in the fact that the moment in dioxane increases from 6.40 D at 25° to about 6.6 D at 70°.

However, it is advisable to consider only qualitatively any moment value in which more than two rotators are involved. For this reason there are numerous entries in Table III for which no calculations are attempted. However, a typical example may be chosen in the observed moment of 3-↓-acetoxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric chloride (3.6 D, III). When the accepted value (1.80 D) for the acetoxy group (26) in its *cis* conformation is used with a calculated moment angle of 121° the over-all molecular moment where two rotators are inclined at 120° is 4.0 D. However, the discrepancy may be made to disappear and then to reappear in a moment value lower than that observed by alteration in the rotations at the ether linkage and the carbonyl linkage in the acetoxy group. Since the anharmonicity of these rotators is unknown, the calculation is of little significance.

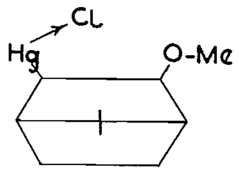
The moment calculation for 3-↓-methoxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric chloride (IV) is more propitious because only two rotators are involved. The rotation is assumed to be harmonic. One rotator is C—Hg—Cl with a group moment of 3.67 D and moment angle 79° from C—Hg. The other rotator is a combined norbornane plus methoxyl moment ($\mu_g = 1.30+0.43\cos 55° = 1.59$ D). The rotator axes are separated by 65°. The resultant is 4.12 D, slightly low by comparison with the observed moment of 4.22 D. This discrepancy may be attributed to anharmonicity such as was postulated for the 2,3-↓↓-dicarboxy analogue (X) because of slight steric hindrance.

When μ for 3-↓-methoxy-1,4-↑↑-methylenecyclohexyl-2-↓-mercuric chloride (VI) is calculated on the same free-rotatory basis as is the diastereomer, IV, the value, 3.4 D, is considerably higher than has been measured (2.88 D). However, a consideration of the quadrant conformations shows that XXXIV surely is excluded on the basis of hindrance between chloromercuri and methoxy. Probably XXXII is excluded for the same reason. The average calculated moment due to XXXI and XXXIII is 2.86 D, in agreement with the observed value.

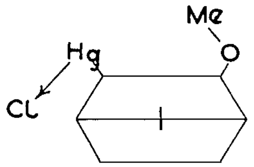
The reasonable adjustments which have been made in calculation are required to bring the norbornane oxymercurials of unknown configuration into correlation with the known configuration of the norbornane dicarboxylic acid mercurials. However, these adjustments have a further significance because those diastereomers (↓↓) in which hindrance is assumed to exist are also the ones which are most easily deoxymercurated.



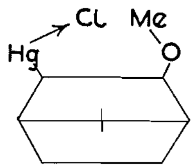
XXXI
$\mu=3.34$



XXXII
$\mu=3.11$



XXXIII
$\mu=2.59$



XXXIV
$\mu=4.44$

The mechanism of deoxymercuration has been suggested variously as due to polar (27) and steric effects (28), and both probably are operative. Certainly the extreme resistance of alkylmercuric halides and the moderate resistance of arylmercuric halides toward demercuration, in contrast to comparatively easy deoxymercuration, shows that polarity of substituents is significant. The static aspects of steric effect have been shown by experiment to be profound. Additionally, and related both to polarity and geometry, are the internal degrees of freedom. The acceptance of the deoxymercurating agent either by co-ordination with the oxy group (polar mechanism) or in concerted cyclic transition states (steric (28)) must be related to molecular flexibility. The rigidity imparted by the norbornane cage makes it possible to correlate the moment values with the ease of deoxymercuration and thus to justify the behavior of 5-↓-hydroxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic acid, γ-lactone (XI), and the simpler mercurial, VI, which is configurationally related to it.

In summary, the calculations show that since the dipole moment of 5-↓-hydroxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic acid, γ-lactone (XI, the configuration of which is known), is lower than that of 5-↓-hydroxy-6-↑-chloromercuri-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic acid, γ-lactone (X), the moment of the norbornene methoxymercurial (which is higher than that of the diastereomer to which it may be rearranged) designates it as 3-↓-methoxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric chloride. The addition of the elements of methoxymercuric salts to norbornene thus occurs in the ↓↑ (so-called *trans*) manner. In part, this is true for oxymercuration of all norbornenes except 1,4-↑↑-methylene-Δ^5-cyclohexene-2,3-↓↓-dicarboxylic acid (VII). The oxymercuration of all norbornenes seems to be acid-catalyzed. This catalysis as well as the ultimate configuration indicates that oxymercuration of norbornenes occurs by an ionic mechanism which may be expressed in terms of a cationic intermediate such as the alkene–mercurinium ion postulated by Lucas, Hepner, and Winstein (3).

But the oxymercuration of cyclohexene, for which this postulate was made, is neither acid-catalyzed nor does the product resemble the oxymercurial from norbornene in respect of moment magnitude and resistance toward deoxymercuration. The same dissimilarity applies to the oxymercurials of cyclopentene, α-terpineol, and also of the stilbenes if conformational aspects are taken into consideration. Although the postulation of Lucas, Hepner, and Winstein seems to apply to a bicyclic alkene in which electron field distortion is probable, this postulation is unrealistic in respect of the conformationally restricted type of alkene for which it was promulgated. The latter type seems to be oxymercurated by a molecular mechanism which causes ↓↓ (so-called *cis*) addition. However, ↑↓ oxymercuration might be found to occur among α,β-unsaturated carbonyl compounds.

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EXPERIMENTAL

Physical Constants

Melting points have been corrected against reliable standards (29). 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 Å. Temperature composition diagrams have been determined (1° per minute) by the method of Rheinboldt and Kirscheim (30). Electrical polarizations in dioxane solutions were made with the apparatus and method described previously (31), and no value of $\Delta\epsilon/\omega_2$ or $\Delta\bar{V}/\omega_2$ was accepted unless the extrapolation matched the ϵ and $\bar{V}$ for pure dioxane. Distortion polarizations were determined from compressed pellets and/or additive group refractions.

Purification of Reagents

The norbornene (1,4-↑↑-methylene-Δ^2-cyclohexene, 100 g) was shaken twice at 50° with 200 ml of 5% aqueous ferrous sulphate in a separatory funnel under nitrogen, then twice with 50-ml portions of water. After it was dried under nitrogen with magnesium sulphate the norbornene was distilled under nitrogen at 95–97°, then fractionated under nitrogen in a 100-plate column, reflux ratio 1:35, b.p. 97–98°, m.p. 45–47°. The mercuric acetate was crystallized from acetic acid (2.5 ml per g) and was washed with anhydrous ether until the odor of acetic acid no longer could be detected.

3-↓-Hydroxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric Chloride (IV, R = H, X = Cl)

A system consisting of 0.94 g (0.01 mole) of norbornene with 3.18 g (0.01 mole) of mercuric acetate and 0.2 ml of concentrated nitric acid in 35 ml of water was allowed to react 1 day and then was treated with aqueous sodium chloride. The product (88%) melted at 124–128° and was purified for analysis (see Table IV) by crystallization from 1:1 ethanol–water. When the nitric acid was not included the crude melting point was 119–125° and treatment with alkali was required to saponify the acetate which was present as an impurity. The other derivatives of Table IV were prepared by treatment with the appropriate sodium halide.

3-↓-Acetoxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric Acetate (III, X = OAc)

To 6.36 g (0.02 mole) of mercuric acetate suspended in 30 ml of 2,5-dioxahexane was added 1.88 g (0.02 mole) of norbornene. After 5.5 hours the insoluble substance was filtered off and washed with 30 ml of dioxahexane, 6.55 g (79%), m.p. 98–100°. The substance was obtained in 84% yield by use of acetic anhydride as the reaction medium (32). Calc. for $C_{11}H_{16}HgO_4$: Hg, 48.7. Found: Hg, 49.3.

4-↓-Acetoxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric Chloride (III, X = Cl)

(*a*) *By Acetylation*

To 2 ml of anhydrous pyridine was added 0.5 g (0.0014 mole) of 3-↓-hydroxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric chloride. To this solution was added 1 ml (0.0065 mole) of acetic anhydride. After 2 days at room temperature the system was poured into 20 ml of cold 5% aqueous sodium chloride. The slowly solidifying product (0.56 g, 98%) melted at 122–124°. After two crystallizations from acetone the melting point (130°) of the product was not depressed by a sample prepared according to procedure (*b*). The substance was found by flotation in thallium formate – malonate at 5° to have a density of 2.37.

(*b*) *By Salt Exchange*

The compound may be obtained in 8% yield by dilution of the mother liquors from the acetate (see above) with aqueous sodium chloride. Alternatively, 1.04 g (0.0025 mole) of 3-↓-acetoxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric acetate was shaken with 25 ml of 5% aqueous sodium chloride for 2 hours, converting it to 0.87 g (88%) of the chloromercurial, m.p. 124–128°. Crystallization from acetone (7 ml per g) raised this melting point to 130.8–131.8° (0.63 g).

The X-ray diffraction pattern was determined: [10] 14.40; [7] 4.77, 4.27, 3.86, 3.53, 2.79; [6] 5.71, 2.41; [5] 5.27, 3.12, 2.47; [4] 8.58, 5.90, 4.00, 3.62, 3.06, 2.98, 2.90, 2.51, 2.25; [3] 3.41, 3.25, 2.66, 2.62, 2.35, 2.31, 2.14; [2] 4.13, 2.19, 2.10, 1.96, 1.93, 1.86, 1.81, 1.77; [1] 7.02, 3.34, 2.27, 2.06, 2.00, 1.72, 1.64, 1.36, 1.24, 1.34; [0.5] 4.95, 2.85. Calc. for $C_9H_{13}ClHgO_2$: C, 27.8; H, 3.34; Hg, 51.6. Found: C, 28.0; H, 3.47; Hg, 52.0.

(*c*) *From Norbornene*

To 5 ml of anhydrous peroxide-free 2,5-dioxahexane was added 0.4 g (0.0017 mole) of mercuric acetate with or without a catalyst. To this suspension was added 0.11 g (0.0017 mole) of norbornene and the system was agitated for 4.5 hours, then filtered into 15 ml of 5% aqueous sodium chloride. After 1.5 hours, filtration with water-washing gave 0.65 g (98%), m.p. 126–128°, when no catalyst was added. Addition of boron fluoride etherate depressed the melting point but not the yield. Addition of 0.00017 mole of pyridine depressed both (62%, m.p. 122–155°) while 0.0017 mole of this retarder depressed both to 24%, m.p. 121–125°. Under the latter conditions a prolonged reaction time (11 hours) increased this low yield to 41%, m.p. 122–124°. The catalytic effect of an equivalent of methanol was found to be negative since a yield of 70%, m.p. 120–125°, was obtained. None of these products gave a melting point depression upon admixture with the purified product of procedures (*a*) and (*b*). Reaction in glacial acetic acid (15 ml) was more rapid than in dioxahexane. The clear solution, after 30 minutes, was drowned in 30 ml of 5% aqueous sodium chloride giving a quantitative yield, m.p. 127–129°. Two crystallizations from acetone (6 ml per g) raised this melting point to 130°.

3-↓-Methoxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric Chloride (IV, R = Me, X = Cl)

(*a*) *By Methylation*

From a 250-ml claisen flask containing 80 ml of sulphur-free toluene was distilled 15 ml to remove water. Then 0.59 g (0.015 atom) of potassium and 10 ml of sodium-dried *tert*-butyl alcohol was added. When solution was complete the excess of *tert*-butyl alcohol was distilled off. Then 1.8 g (0.005 mole) of 3-↓-hydroxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric chloride was dissolved in the stirred system. After 90 minutes the whole was partially vacuum-distilled to remove *tert*-butyl alcohol. To the remainder was added 1.89 g (0.015 mole) of pure dimethyl sulphate. After the solution was stirred for 90 minutes 40 ml of 10% aqueous sodium hydroxide was added. The remaining toluene was vacuum-distilled off after 15 minutes. The residue, diluted with 90 ml of 1.5% aqueous sodium chloride, was treated exhaustively with gaseous carbon dioxide. The precipitate, 1.4 g (77%), m.p. 119–122°, was crystallized from absolute ethanol, m.p. 121–123°. A mixture melting point with the methoxymercurial prepared according to procedure (*b*) or by Rowland's procedure (8) was not lowered. The density, determined by flotation at 5° in an aqueous thallium formate – malonate solution, was 2.41. Oxidation with alkaline permanganate was difficult and much unchanged mercurial was recovered. However, a 10% yield of 1,3-↓↓-cyclopentanedicarboxylic acid, m.p. 119°, was obtained.

(*b*) *By Standard Oxymercuration*

To 10 ml of absolute methanol containing the catalyst (see Table II) was added 0.23 g (0.0025 mole) of norbornene. To the homogeneous solution was added with shaking 0.80 g (0.0025 mole) of mercuric acetate. The homogeneous reaction continued for 90 minutes; then the system was chilled to 5° and this temperature was maintained while 20 ml of 5% aqueous sodium chloride was added. The system kept at 5° during 2 hours was filtered, washed with water, and vacuum-dried. The typical yield with 0.5 equivalent of boron fluoride was 0.85 g (95%), m.p. 115–118°, or with 0.2 equivalent of ferrous sulphate was 95%, m.p. 108–114°. The product was analyzed as described below or was crystallized from hot carbon tetrachloride (1 ml per g), m.p. 120–121°. Melting point ranges were determined in the Rheinboldt apparatus, the temperature–composition diagram having been determined from known mixtures of methoxy- and acetoxy-mercurials which were together dissolved in chloroform and evaporated. The acetyl content of the known mixtures and the products were determined by the method of Friedrich (33).

(*c*) *From Mercuric Chloride*

A mixture of 0.94 g (0.01 mole) of norbornene and 2.71 g (0.01 mole) of mercuric chloride in 25 ml of methanol was maintained for 10 hours and then chilled to −60° and filtered to remove 0.67 g, m.p. 89.5–91.5°, which contained 0.30 g of benzene-insoluble mercuric chloride. The filtrate was diluted to a volume of 45 ml and was filtered quickly, 0.49 g, m.p. 121–122°. The total yield (0.86 g, 24%) was crystallized from 2:1 hexane–benzene, m.p. 122–123°. A mixture melting point with the pure products of procedures (*a*) and (*b*) was not lowered.

(*d*) *By Mercuric Acetate plus Mercuric Oxide*

Suspensions of 10 ml of absolute methanol, 0.80 g (0.0025 mole) of mercuric acetate, and 0.10 g (0.0005 mole) of alkali-free yellow mercuric oxide were stirred under reflux in nitrogen for 8 hours. Each was then stirred for various periods of time after 0.23 g (0.0025 mole) of norbornene was added, then was chilled and treated with 20 ml of 5% aqueous sodium chloride and chilled to 5° overnight. The yield after 15 minutes and also after 4 hours was 70%, m.p. 92–101°, but after 12 hours it was 90%, m.p. 92–106°, indicating a retarded formation of methoxymercurial. The marked acceleration after 4 hours undoubtedly is related to the disappearance of suspended material after this time interval.

TABLE IV

Preparation and properties of 2-↓-alkoxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric halides (IV) from equimolar amounts of norbornene (I) and mercuric acetate in the protonic medium (ROH), then treated with alkali halides (MX)

Properties	R = H X = Cl	R = H X = Br	R = H X = I	R = Me X = Cl	R = Me X = Br	R = Et X = Cl	R = Et X = Br
Yield	88	90	93	91	97	78	93
M.p., ° C	128.6–129.3	130.7–131.2	146.6–147.2	123.0–123.7	89.3–89.8	64–65	80.4–81.2
% C:							
calc.	24.2	21.4	19.2	26.6	23.7	28.8	25.8
found	24.5	21.3	19.1	26.7	23.5	28.6	25.2
% H:							
calc.	3.20	2.81	2.52	3.63	3.20	4.01	3.58
found	3.62	2.99	2.57	3.77	3.40	4.17	3.44
% Hg:							
calc.	57.8			55.6		53.6	
found	57.6			56.2		53.5	
X-ray diagram							
[10]	8.63			9.50		13.80	
[9]	4.78			6.06		3.65	
[8]	5.12 3.31 3.51			5.12 4.95 3.56		5.57 4.55 3.42	
[7]	2.92 2.58 3.08			2.93 3.70 3.93		8.50 5.61 5.34	
[6]	2.80 2.54			3.35 3.06		4.30 4.20	
[5]	2.45 2.15 2.03 1.98			3.48 2.62 2.51 2.24		6.94 6.53 5.05 4.10	

2,2′-↑↑-Mercuri-bis-3-↓-methoxy-1,4-↑↑-methylenecyclohexane (V, *dd,ll and* V, *dl,ld*)

To 100 ml of 85% hydrazine hydrate chilled to −70° was added 27 g (0.0075 mole) of 3-↓-methoxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric chloride. The temperature was allowed to rise slowly to that of the ice bath into which the system was transferred. After 20 minutes a pink color was observed which changed to blue-black. After 12 hours at 25° the whole was heated on the steam bath for 3 hours, then chilled for 12 hours.

The aqueous layer and the metallic mercury were decanted from the white solid (12 g, 70%, m.p. 70–110°) which was heated with 100 ml more of hydrazine hydrate on the steam bath for 11 hours. Chilling yielded 4.3 g (25%) of crude product, m.p. 62–66°, softening at 55°. The same color change and the same yield, but with lower melting point (56.2–57.5°), may be obtained if 1 mole of mercurial in 5 moles of 2.5% aqueous alkali is treated with 0.5 mole of stannous chloride dihydrate during 24 hours.

This mixture of two diastereomers may be separated by 'triangular' crystallization utilizing methanol in which the higher melting isomer is relatively insoluble and methanol–water from which the lower melting isomer may be crystallized. Finally the higher melting isomer was crystallized from acetone, m.p. 107.5–108°. The lower melting isomer finally was crystallized from methanol, m.p. 66–66.5°. The ratio of high to low was found to be 6 to 1. Calc. for $C_{16}H_{26}O_2Hg$: C, 42.7; H, 5.76. Found (high): C, 42.8; H, 5.73. Found (low): C, 42.7; H, 5.67. The X-ray pattern for the high melting diastereomer was [10] 10.64, 10.00, 5.82, 5.60; [6] 4.21, 3.87, 3.77, 3.47, 3.26; [4] 2.74, 2.65, 2.22, while that of the low melting isomer was [10] 11.33, 5.34, 4.79; [9] 7.76, 7.53, 3.90; [8] 3.61, 3.46; [6] 3.09, 3.02, 2.68, 2.59, 2.36, 2.40; [3] 2.15, 2.10.

When either the high or low melting isomer was refluxed for 3 hours with 2 equivalents of mercuric acetate in methanol, and then was treated with sodium chloride, the crude chloromercurials melted at 120–122°. A mixture melting point with 3-↓-methoxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric chloride was not lowered. In each instance about 10% of bis-mercurial was recovered unchanged. The same chloromercurial, m.p. 121–122°, was obtained when either isomer was treated with methanolic hydrochloric acid for 5 minutes. Either isomer could be heated to 115° for 40 minutes without change.

An unsuccessful attempt was made to synthesize the bis-mercuri diastereomers by converting 0.9 g (0.0025 mole) of 3-↓-methoxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric chloride either to the organomercuric acetate by 0.41 g of silver acetate or to the organomercuric hydroxide by treatment with silver oxide, both in methanol, followed by treatment with norbornene (0.47 g, 0.005 mole) and 12 mg of boron fluoride etherate. After 1 day the original mercurials were recovered unchanged.

1,4-↑↑-Methylenecyclohexan-↓-yl Phenylurethane

To 1.40 g (0.004 mole) of 3-↓-hydroxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric chloride in 18 ml of methanol was added a solution of 0.32 g (0.008 mole) of sodium hydroxide in 1 ml of distilled water. This solution was refluxed 6 hours with 0.47 ml (0.008 mole) of 85% hydrazine hydrate; 0.70 g (87%) of the mercury was filtered off as the metal.

The filtrate, diluted with 75 ml of water, was ethyl ether-extracted (75 ml) and the extract was evaporated to 5 ml. The solid which crystallized, m.p. 151–152°, 0.28 g (62%), was 2-hydroxy-1,4-↑↑-methylenecyclohexane (no mercury). A mixture melting point with an authentic sample of 2-↓-hydroxy-1,4-↑↑-methylenecyclohexane (34) gave no depression. A 0.01-g (0.0009 mole) portion of the alcohol was treated with 1 equivalent of phenyl isocyanate in 3 ml of hexane for 1 day. The urethane, 0.15 g (60%), melted at 158–159° before and 160–161° after crystallization from benzene, mixture melting point not lowered.

3-↓-Methoxy-1,4-↑↑-methylenecyclohexyl-2-↓-mercuric Chloride (VI)

To 25.2 g (0.07 mole) of 3-↓-methoxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric chloride (IV, R = Me, X = Cl) in 750 ml of water plus 5.60 g (0.14 mole) of sodium hydroxide was added 0.3 g of 100% hydrazine hydrate. After 6 hours the cooled system was ether-extracted (30 ml) and the aqueous, metallic, and non-aqueous phases were separated. The aqueous phase was acidified with acetic acid to yield a variable amount of original mercurial admixed with bis-mercurial and product, m.p. 78–95°, mixture melting point with original mercurial 80–110°, maximum amount 12.1 g (48%).

The non-aqueous phase was evaporated leaving an oil, 4.80 g, which was dissolved in 35 ml of hot methanol. Then 2 ml of concentrated hydrochloric acid was added to the slightly warm solution. After 30 minutes at room temperature water was added to turbidity. The system was extracted by chloroform and this extract was vacuum-evaporated leaving 1.80 g of semisolid which was crystallized from carbon tetrachloride (11 ml per g), 1.5 g, m.p. 113–114°, 6% yield. Crystallization from absolute ethanol (30 ml per g) raised this melting point to 117.7–118.5°, recovery 45%. A mixture melting point with the original mercurial was lowered to 80–85°. Diffraction pattern: [10] 11.62; [8] 5.14, 4.14, 3.37, 3.14; [6] 6.91, 6.28, 5.21; [5] 3.09; [4] 3.87, 3.46, 2.15, 2.10. Calc. for $C_6H_{13}ClHgO$: C, 26.6; H, 3.63; Hg, 55.6. Found: C, 26.7; H, 3.74; Hg, 55.0.

In a variation the concentrate from the non-aqueous extract of the reaction system was shaken for 15 minutes with 150 ml of 10% hydrochloric acid. The gummy solid was dissolved in 125 ml of absolute ethanol, and 2 ml of 5% aqueous sodium chloride was added. After 30 minutes a precipitate appeared (m.p. 110–112°, yield 12%), which was purified to m.p. 117.5–118.5° as described above.

A mixture of this ↓↓-diastereomer and the ↑↓-diastereomer from which it was formed (0.1 g of each in 10 ml of methanol) was treated with 0.2 ml of hydrochloric acid for 40 minutes. Addition of sodium hydroxide precipitated mercuric oxide which was filtered off. The filtrate, upon acidification with acetic acid, precipitated 0.06 g (30%), m.p. 112–117°. Crystallization from absolute ethanol raised this melting point to 120–122°. A mixture melting point with the ↓↓-diastereomer was lowered to 95° while no depression was observed upon admixture with the ↑↓-diastereomer.

2-↓-Methoxy-1,4-↑↑-methylenecyclohexane

A suspension of 11 g (0.03 mole) of 3-↓-methoxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric chloride in 50 ml of water was shaken slowly and 100 g (0.1 atom) of 2% sodium amalgam was added. After 12 hours the system was steam-distilled and the non-aqueous phase of the distillate was dried with magnesium sulphate and distilled, b.p. 59–62°, at 30 mm, 1.90 g (50%), n_D^{20} 1.4574. It was redistilled, b.p. 154–155°, at 750 mm, n_D^{20} 1.4572. This product could not be frozen at −80° C. The same product was obtained by reduction of 3-↓-methoxy-1,4-↑↑-methylenecyclohexyl-2-↑-mercuric chloride with an excess of hydrazine hydrate and by methylation of 2-↓-hydroxy-1,4-↑↑-methylenecyclohexane in diethyl ether by use of sodamide and methyl iodide. Calc. for $C_8H_{14}O$: C, 76.1; H, 11.25; OCH_3, 24.6. Found: C, 76.1; H, 11.17; OCH_3, 25.1.

5-↓-Hydroxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic Acid, γ-Lactone, $\mu = 3.88$ D (XI)

A solution of 1.82 g (0.01 mole) of 1,4-↑↑-methylene-Δ^5-cyclohexene-2,3-↓↓-dicarboxylic acid in 50 ml of water at 80° was agitated while 2.70 g (0.01 mole) of mercuric chloride dissolved rapidly. The product appeared within 6 seconds and was filtered off when the system was cool, m.p. 202°, 3.97 g (95%). By crystallization via solution in dimethylformamide and gradual precipitation with chloroform (the first slight precipitate being discarded) it melted at 225–226° when inserted about 10° below this melting point. The X-ray diffraction pattern was [10] 4.55; [9] 4.74; [8] 4.00; [7] 6.13, 6.57, 7.25; [5] 2.78; [4] 3.50; [3] 2.57; [2] 2.88, 2.98; [1] 5.51, 3.06; [0.5] 4.16, 3.43.

A repetition of this experiment in which 2 ml (0.02 mole) of concentrated hydrochloric acid was included showed that the reaction was retarded both with respect to time of appearance of product and disappearance of inorganic mercury. However, the ultimate yield was 2.68 g (89%). The delay was still longer (20 minutes) before the first precipitate appeared when 4 ml (0.04 mole) of hydrochloric acid was included and the final yield after 1 day was 75%. Conversely the inclusion of 4 ml (0.01 mole) of 10% aqueous sodium hydroxide in the system reduced the time for appearance of product to 3 seconds; the ultimate yield was 93%.

5-↓-Hydroxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2-↓-3-↑-dicarboxylic Acid, $\mu = 4.07$ (XII)

(*a*) *By Isomerization of* XI (*$\mu = 3.88$ D*)

A solution of 41.7 g (0.10 mole) of 5-↓-hydroxy-6-↓-chloromercuri-1,4-↑↑-methylene-2,3-↓↓-dicarboxylic acid ($\mu = 3.88$) in 400 ml (1.0 mole) of 10% aqueous sodium hydroxide was refluxed for 2 hours, then cooled slowly, finally chilled and acidified by acetic acid to pH 5. The precipitate, 12.65 g of impure diastereomer, $\mu = 3.88$, melted at about 200°. The filtrate was made basic to pH 7.5, then was vacuum-evaporated to a 100-ml volume, and then was acidified cold to pH 2 with hydrochloric acid. The 15-g crop, m.p. about 190°, was dissolved in 50 ml of dimethylformamide, filtered, and treated with 80 ml of chloroform. After a precipitate (10 g, m.p. 206°) was filtered off, the filtrate was vacuum-evaporated. The residue was crystallized from 250 ml of boiling water to give 5 g (12%), m.p. 219–219.5°, strongly depressed by admixture with the diastereomer: μ, 3.88. Recrystallization from dimethylformamide–chloroform or from boiling water raised this melting point to 223–223.5° (sample inserted at 215°). Calc. for $C_9H_{11}O_5HgCl$: C, 24.8; H, 2.54. Found: C, 25.0; H, 2.75. The X-ray diffraction pattern was found to be [10] 12.10; [9] 5.12; [8] 3.56; [7] 3.07; [6] 4.67; [5] 6.23; [4] 6.65, 3.97; [3] 10.9, 5.94. The substance largely survived treatment with concentrated hydrochloric acid for 5 minutes but during 50 minutes it was converted to 1,4-↑↑-methylene-Δ^5-cyclohexene-2,3-↑↓-dicarboxylic acid (XIII), m.p. 184–185°, not depressed by mixture melting point with an authentic sample.

When the mercurial, $\mu = 4.07$, was dissolved in cold alkali and potentiometrically titrated with standard hydrochloric acid it showed by three inflections (corresponding with 3 equivalents) that the substance was not a lactone. Treatment with acetic anhydride failed to convert this hydroxydicarboxylic acid to a γ-lactone.

(*b*) *By Oxymercuration of* XIII

A solution of 76.7 g (0.38 mole) of 1,4-↑↑-methylene-Δ^5-cyclohexene-2-↓-3-↑-dicarboxylic acid (XIII) in 3 liters of boiling water was treated with 103 g (0.38 mole) of mercuric chloride. The precipitating system was cooled to 25°, and then 300 ml (0.75 mole) of 10% aqueous sodium hydroxide was added (pH 5). After 8 hours the system was acidified to pH 2. The precipitate was filtered off, washed with methanol and ether, and then vacuum-dried, 145 g, m.p. 211–212°. This crude product was extracted with 1300 ml of boiling water leaving 132 g, m.p. 222–223°. A hot solution in dioxane (10 ml per g) precipitated about 70%, m.p. 217°. The remaining 30% was obtained from the filtrate by addition of an equal volume of diethyl ether and was nearly pure XII, m.p. 218–219°. The process should be repeated with the 70%, m.p. 217°, which yields less pure XII, m.p. 213–214°. All of the crops of XII (estimated total yield, 25%) may be purified by crystallization from boiling water (10 ml per g), m.p. 220–221°.

The aqueous filtrates and the initial precipitates from dioxane crystallizations are rich in XIV. After the latter had been removed as is described below the final aqueous filtrates yielded about 20 g of unchanged norbornenedicarboxylic acid, XIII.

5-↓-Hydroxy-6-↓-hydroxymercuri-1,4-↑↑-methylenecyclohexane-2-↓-3-↑-dicarboxylic Acid

A solution of 2.15 g (0.005 mole) of 5-↓-hydroxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2-↓-3-↑-dicarboxylic acid (XII) in 4 ml (0.01 mole) of 10% aqueous sodium hydroxide was shaken with 0.8 g (0.055 mole) of silver oxide for 2 hours, then filtered by suction to remove a mixture of silver oxide and chloride from which 0.70 g (98%) of the chloride was isolated by washing the mixture with nitric acid.

The filtrate from the mixture was acidified to pH 5.6 with acetic acid; the precipitate which appeared momentarily redissolved. When no precipitate appeared after 12 hours the system was further acidified to pH 5 with 10% aqueous acetic acid. The precipitate was filtered off and dissolved in 30 ml of 1% aqueous sodium hydroxide. The solution was clarified by means of Norite, then was filtered, and the filtrate was acidified with acetic acid. After 36 hours at 4° the precipitate was filtered off, 0.70 g (34%), m.p. 198°. Resolution in alkali with Norite treatment gave a solution from which no precipitate appeared upon saturation with carbon dioxide gas. Acidification by acetic acid to pH 5.2 gave a gelatinous precipitate (0.55 g), which was dissolved in alkali, treated with Norite, filtered, and acidified by use of acetic acid, m.p. 200.5–201°. Calc. for $C_9H_{12}O_6Hg$: C, 25.9; H, 2.90. Found: C, 25.8; H, 3.13.

When this substance was dissolved in dilute alkali, and then dilute hydrochloric acid was added, the melting point (221°) of the precipitate was not depressed by admixture with 5-↓-hydroxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2-↓-3-↑-dicarboxylic acid (XII).

5-↓-Hydroxy-1,4-↑↑-methylenecyclohexane-2-↓-3-↑-dicarboxylic Acid

A solution of 1.08 g (0.0025 mole) of 5-↓-hydroxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2-↓-3-↑-dicarboxylic acid (XII) in 4 ml (0.005 mole) of 5% aqueous sodium hydroxide was chilled to 4°, and 6.5 g (0.01 atom Na) of sodium amalgam was added at once. Next day the system was filtered and the chilled filtrate was acidified with concentrated hydrochloric acid. The crystalline precipitate (0.24 g) melted at 210–211°, decomp. The chilled filtrate after 5 days yielded 0.12 g, m.p. 209–210° (total 72%). The whole was crystallized from 1.5 ml of hot water and also from hot ethyl acetate, m.p. 210–211°, decomp. A mixture melting point with 5-↑-hydroxy-1,4-↑↑-methylenecyclohexane-2-↓-3-↑-dicarboxylic acid was lowered to 192°. Calc. for $C_9H_{12}O_5$: C, 54.1; H, 6.04. Found: C, 54.1; H, 6.14. The X-ray diffraction pattern is [10] 5.30; [9] 4.38, 4.79; [8] 3.38; [6] 5.68, 3.65; [5] 4.23; [4] 5.98; [3] 3.79, 2.70, 3.22; [2] 2.79, 2.97; [1] 2.16, 2.00, 2.50.

5-↓-Hydroxy-6-↑-chloromercuri-1,4-↑↑-cyclohexane-2-↑-3-↓-dicarboxylic Acid, γ-Lactone, μ = *6.40* (XIV)

(*a*) *By Oxymercuration*

After the product obtained by treatment of 0.38 mole of 1,4-↑↑-methylene-Δ^5-cyclohexene-2-↓-3-↑-dicarboxylic acid was extracted to remove XII there remained impure crops (m.p. 208–213°) from dioxane crystallizations, and also filtrates from aqueous extractions and crystallizations. The latter were vacuum-evaporated and the whole was dissolved in hot water (10 ml per g), cooled, and filtered. Evaporation of the filtrates to 1/2–1/3 volume gave precipitates of XIV melting at 228–236°. These crops represent a total isolable yield of about 40% of theoretical. The final purification was effected by crystallization from hot dioxane (23 ml per g), m.p. 237–238°. Calc. for $C_9H_9ClHgO_4$: C, 25.7; H, 2.18. Found: C, 25.3; H, 2.43. The X-ray diffraction pattern was [10] 13.5; [9] 8.97; [8] 7.29; [7] 10.45; [4] 3.66; [3] 4.27; [2] 6.19, 5.04; [1] 3.01. Treatment for 1 hour with twice its weight of concentrated hydrochloric acid converted the mercurial into 1,4-↑↑-methylene-Δ^5-cyclohexene-2-↓-3-↑-dicarboxylic acid, m.p. 186–187°, authenticated by mixture melting point.

When a solution of 150 mg of this mercurial (μ = 6.40 D) and 150 mg of 5-↓-hydroxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2-↓-3-↑-dicarboxylic acid (μ = 4.07 D) in 80 ml of dioxane was treated with 0.5 ml of concentrated hydrochloric acid for 3 hours the vacuum-evaporated system could be extracted with chloroform to yield only one mercurial, which, crystallized from water, melted at 230°, 60 mg, with powder diagram identical with that shown above for the compound, μ = 6.40 D. The chloroform-insoluble portion yielded 1,4-↑↑-methylene-Δ^5-cyclohexene-2-↓-3-↑-dicarboxylic acid, m.p. 186–187°, with X-ray powder diagram [10] 4.99; [5] 4.34; [4] 3.92; [2] 4.61, 4.51, 3.44, 3.19; [1] 6.43, 5.62, 3.01, 2.95, 2.68. This pattern is in contrast to that determined for 1,4-↑↑-methylene-Δ^5-cyclohexene-2,3-↓↓-dicarboxylic acid, m.p. 179–180°, which is [10] 6.10; [9] 4.44; [8] 4.23; [5] 4.95; [3] 3.86, 3.25; [2] 2.79, 2.73; [1] 5.47, 5.18, 5.06, 3.49, 2.39. The reader is cautioned about the subtle difference between this latter pattern and that of the product of platinum-catalyzed reduction, 1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic acid, m.p. 161–161.5°: [10] 6.25; [9] 4.45; [8] 4.32; [5] 5.05; [3] 3.91, 3.35, 3.27, 2.79, 2.48; [2] 5.23; [1] 5.62, 5.45, 3.82, 2.93, 2.72.

A solution of 0.86 g (0.002 mole) of 5-↓-hydroxy-6-↑-chloromercuri-1,4-↑↑-methylenecyclohexane-2-↑-3-↓-dicarboxylic acid, γ-lactone, in 4 ml (0.005 mole) of 5% aqueous sodium hydroxide was chilled and treated at once with 5.2 g (0.008 atom Na) of 3.5% sodium amalgam. After 7 hours the system was filtered and the chilled filtrate was acidified strongly with concentrated hydrochloric acid. The crystals, 0.25 g, m.p. 127–128° (70%), were recrystallized from benzene (50 ml per g), m.p. 132–133.5°. A mixture melting point with 5-↓-hydroxy-1,4-↑↑-methylenecyclohexane-2-↑-3-↓-dicarboxylic acid, γ-lactone, was not depressed.

(*b*) *By Isomerization*

A mixture of 1.82 g (0.0032 mole) of 5-↓-hydroxy-6-↑-chloromercuri-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic acid, γ-lactone (X, μ = 7.18), and 0.82 g (0.0032 mole) of mercurous acetate in 25 ml of methanol was refluxed for 8 hours. Then it was diluted with water and made slightly alkaline. Darco was added and the dirty yellow precipitate was filtered off. The filtrate was acidified by addition of acetic acid to yield 1.00 g of chloride-free precipitate of indistinct melting point.

This precipitate was refluxed 3 hours in 20 ml of 4% aqueous sodium hydroxide, then chilled and acidified to pH 5.0 by addition of acetic acid. After 12 hours 0.48 g of infusible precipitate was filtered off. The filtrate upon acidification to pH 2 with dilute hydrochloric acid yielded 0.22 g, m.p. 233–235°, not depressed by admixture with the mercurial, μ = 6.40, prepared by oxymercuration, but was depressed by the mercurials X (μ = 7.18) and XII (μ = 4.07).

The infusible precipitate, 0.48 g, was dissolved in 10% aqueous sodium chloride and then was acidified with 12% hydrochloric acid. The precipitate, m.p. 211–213°, was crystallized from water, m.p. 223–224°, not depressed by admixture with the reagent mercurial, X.

5-↓-Hydroxy-6-↑-chloromercuri-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic Acid, γ-Lactone, μ = 7.18 D (X)

To a solution of 1.13 g (0.005 mole) of stannous chloride dihydrate in 50 ml (0.02 mole) of 1.6% aqueous sodium hydroxide was added 4.00 g (0.01 mole) of 5-↓-hydroxy-anhydro-[6-↓-hydroxymercuri-2-↓-carboxy]-1,4-↑↑-methylenecyclohexane-3-↓-carboxylic acid (11) and then 2.7 cc (0.0068 mole) more of aqueous 10% sodium hydroxide; final pH was 8. After 1 hour the black precipitate was filtered off. The cold filtrate was strongly and quickly acidified with 12% hydrochloric acid in order to redissolve the precipitated tin salts; then a granular precipitate appeared. After 12 hours the precipitate was filtered off and washed with water, 1.95 g (47%), m.p. 204–205°. Crystallization from methanol (0.6 g per ml, Darco) raised this melting point to 225.5–226°. Mixture melting points with the mercurials of moments of 3.88, 4.07, and 6.40 D all were depressed. X-Ray diffraction pattern is [10] 6.70; [7] 12.10; [5] 6.15, 5.02, 4.88, 4.00, 3.62, 3.14; [4] 3.32, 2.74, 5.32, 4.38; [1] 4.58, 4.22, 3.07. Calc. for $C_9H_9ClHgO_4$: C, 25.7; H, 2.17. Found: C, 26.2; H, 2.31.

When 0.10 g of this product and of the diastereomeric mercurial, μ = 3.88 D, were mixed and treated with 0.5 ml of concentrated hydrochloric acid for 5 minutes the diluate with an equal volume of water yielded 6 mg with X-ray diffraction pattern corresponding with the product, μ = 7.18 D. When the latter was treated alone with 1.4 times its weight of concentrated hydrochloric acid for 45 minutes at least 30% of it survived, m.p. 216–217°, not depressed by admixture with the pure reagent, μ = 7.18 D. However, a reaction period of 12 hours yielded only 5-↓-hydroxy-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic acid, γ-lactone, m.p. 202°, not depressed by admixture with the authentic lactone (35). The lactone was characterized further by methylation as described below.

5-↓-Hydroxy-2-↓-carbomethoxy-1,4-↑↑-methylenecyclohexane-3-↓-carboxylic Acid, γ-Lactone

A solution of 7.28 g (0.04 mole) of 5-↓-hydroxy-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic acid, γ-lactone, m.p. 201–202°, in 32 ml (0.08 mole) of 10% aqueous sodium hydroxide was heated to boiling for several minutes, then cooled to 25°, and 6.72 g (0.08 mole) of sodium bicarbonate was added in 50 ml of water. Then 15.2 ml (0.16 mole) of dimethyl sulphate was added and the system was stirred for 2 days. The whole was then exhaustively extracted with chloroform. The evaporated extracts were crystallized from water, 4.79 g, 61%, m.p. 76–77°. This product was crystallized from benzene – commercial hexane (1:1, 40 ml per g), m.p. 81–82°. X-Ray diagram was [10] 5.38; [8] 4.73; [6] 6.53; [5] 3.99, 3.50, 3.39; [3] 3.81, 2.85; [2] 5.94, 4.38, 3.27; [1] 7.59, 4.94, 2.27. Calc. for $C_{10}H_{12}O_4$: C, 61.3; H, 6.17. Found: C, 61.3; H, 6.23.

5-↓-Hydroxy-2-↑-carbomethoxy-1,4-↑↑-methylenecyclohexane-3-↓-carboxylic Acid, γ-Lactone

When 1.96 g (0.01 mole) of 5-↓-hydroxy-2-↓-carbomethoxy-1,4-↑↑-methylenecyclohexane-3-↓-carboxylic acid, γ-lactone, m.p. 81–82°, was treated for 45 minutes with a solution of 0.23 g (0.01 atom) of sodium in 15 ml of methanol and then with 0.95 ml (0.01 mole) of dimethyl sulphate a rise in temperature was observed at the last step. After 1 hour the solvent was removed under vacuum and replaced with water. The product (1.46 g, 70%, m.p. 67–68°) was crystallized from boiling ethyl ether (1.2 ml per g), m.p. 68.3–68.8°. X-Ray diagram: [10] 5.15; [9] 4.59; [5] 5.64; [3] 6.60, 4.23; [2] 3.83, 3.46, 2.87; [1] 3.68, 2.58, 2.11. This substance was recovered unchanged after 6 hours with 1 equivalent of 10% aqueous mercuric acetate. When the substance was saponified during 1 hour with 10% aqueous alkali at 80° or was hydrolyzed by concentrated hydrochloric acid during 1 minute it yielded 5-↓-hydroxy-1,4-↑↑-methylenecyclohexane-2-↑-3-↓-dicarboxylic acid, γ-lactone, m.p. 132.8–133°, authentic according to mixture melting point and elemental analysis. Calc. for $C_{10}H_{12}O_4$: C, 61.3; H, 6.17. Found: C, 61.8; H, 6.32.

1,4-↑↑-Methylene-Δ^5-cyclohexene-2,3-↑↓-dicarboxylic Acid (XIII)

When prepared by sodium methoxide saponification of dimethyl 1,4-↑↑-methylene-Δ^5-cyclohexene-2,3-↓↓-dicarboxylate (35) the compound melted at 186.5° after crystallization from hot acetonitrile (25 ml per g). The powder diagram is reported above.

Dimethyl 5-↑-Acetoxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylate (XXIII, Z = CH_3CO, X = Cl)

(*a*) *In 2,5-Dioxahexane*

To a solution of dimethyl 1,4-↑↑-methylene-Δ^5-cyclohexene-2,3-↓↓-dicarboxylate (m.p. 37°, 1.05 g, 0.0047 mole) in 10 ml of anhydrous 2,5-dioxahexane was added 1.45 g (0.0046 mole) of mercuric acetate. After 74 hours of agitation the system (in which all of the solid had dissolved) was poured into 40 ml of 2.5% aqueous sodium chloride. The oil soon crystallized, 1.925 g (83%), m.p. 153–158°. Four crystallizations from methanol raised the melting point to 177°. Diffraction pattern was [10] 5.64; [9] 6.41; [8] 11.47, 6.96; [7] 4.80, 3.88; [6] 3.23; [4] 4.50, 3.66; [3] 4.17, 3.48. Calc. for $C_{13}H_{17}ClHgO_6$: C, 30.9; H, 3.38; OCH_3, 12.3. Found: C, 30.6; H, 3.54; OCH_3, 12.1.

(*b*) *In Methanol*

To 2.10 g (0.01 mole) of the dimethyl ester in 35 ml of anhydrous methanol was added 3.18 g (0.01 mole) of mercuric acetate. The salt dissolved during 25 minutes. After 8 hours the system was filtered into 100 ml of 5% aqueous sodium chloride. The precipitate (4.57 g, 95%, m.p. 163–165°) was crystallized from absolute methanol (25 ml per g), m.p. 171–172°.

(*c*) *In Acetic Acid*

A solution of 10.5 g (0.047 mole) of the ester used in procedure (*a*) and 14.5 g (0.046 mole) of mercuric acetate in 50 ml of glacial acetic acid was let stand for 12 hours, then was poured into 350 ml of 3% aqueous sodium chloride. The precipitate was filtered off after 1 hour, washed with water and with methanol, and vacuum-dried, 22.1 g (93%), m.p. 173–174°. Crystallization from methanol (55 ml per g) raised this melting point to 177–177.2° (11.4 g). Subsequent crops, m.p. 175–168°, obtained by chilling and by concentration of the mother liquor finally left a filtrate which was vacuum-evaporated. The residue was twice purified by solution in warm dimethylformamide (12 ml per g), filtration of the slight precipitate appearing at 25°, and then dilution with an equal volume of chloroform. The product (0.13 g, 0.5%), m.p. 229–229.5°, was found to be 5-↓-hydroxy-6-↓-chloromercuri-2-↓-carbomethoxy-1,4-↑↑-methylenecyclohexane-3-↓-carboxylic acid, γ-lactone (XXII, X = Cl) (11). Identification was made by mixture melting point after it was found that the substance prepared from the ester and mercuric acetate in water also melted at 229° (rather than 223.5°) after sufficient purification. The two products gave the same X-ray powder pattern.

When 3 g of the dimethyl 5-↑-acetoxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2-↓-3-↑-dicarboxylate was reduced by 2 g of lithium aluminum hydride in tetrahydrofuran (slow addition followed by reflux) with hydrolysis by aqueous ammonium chloride, the product, m.p. 78-84°, weight 0.85 g, upon crystallization from commercial pentane melted at 81.5–83°. It reacts rapidly with alkaline permanganate to yield a product which may be 2,3-dimethylol-1,4-↑↑-methylene-Δ^5-cyclohexene.

5-↑-Hydroxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2-↓-3-↑-dicarboxylic Acid (XXIV)

A solution of 5.15 g (0.01 mole) of dimethyl 5-↑-acetoxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylate in 36 ml (0.09 mole) of 10% aqueous sodium hydroxide was maintained at room temperature for 15 hours, then chilled and acidified cautiously to pH 2 with concentrated hydrochloric acid. The precipitation which commenced after 15 minutes was complete after 1 day at 4°. Filtration gave 2.59 g (60%), m.p. 183–184° (inserted at 160°). Quick crystallization from boiling water (10 ml per g) raised this melting point to 184–184.5°. The X-ray diffraction pattern was [10] 4.21, 5.05; [9] 5.79; [8] 5.60; [7] 3.44; [6] 3.26, 3.14; [5] 3.03; [3] 2.39; [2] 2.74; [1] 2.66, 3.91. The infrared band spectrum of polyethylene wax pellets (6000 p.s.i. at 23°) containing 5% is reported in wave numbers [cm^{-1}] at specified per cent transmissions: [316] 46; [352] 82; [388] 85; [410–17] 88; [428] 76; [451] 83; [553] 73; [648] 50; [678] 68; [794] 68; [884] 53. The density of the solid at 23° was 2.420 and the extrapolated dielectric constant of pellets was 3.917, so P_{e+a} is 88.5 cc. Calc. for $C_9H_{11}ClHgO_5$: C, 24.9; H, 2.56. Found: C, 25.0; H, 2.70.

When this substance was dissolved and boiled in water (7–8 ml per g) for 15 minutes the crystals which separated upon cooling melted first at 216–217° and then after an identical crystallization at 221–222°. The X-ray diffraction pattern was [10] 9.65; [9] 5.80; [8] 3.64; [7] 7.22; [6] 4.21, 4.25; [5] 4.56, 4.83, 5.26; [4] 3.22, 3.07; [3] 3.35, 3.50; [2] 2.94; [1] 2.82. The infrared band spectrum (5% in polyethylene wax compressed at 6000 p.s.i.) was recorded in [cm^{-1}] at indicated per cent transmissions: [316.8] 42; [351] 75; [390] 76; [414] 76; [429] 66; [453] 71; [550] 58; [649] 42; [675] 54; [696–702] 55; [791] 42; [841] 40; [881] 35. The density of the solid substance at 23° was 2.453 and the dielectric constants of pellets of various thicknesses were extrapolated to zero thickness for $\epsilon = 4.019$, whence P_{e+a} is 88.9 cc. Calc. for $C_9H_{11}ClHgO_5$: C, 24.9; H, 2.56. Found: C, 24.7; H, 2.53.

The melting point was not depressed when the substance was quickly crystallized from water or other solvents, but when it was dissolved in alkali and then reprecipitated by addition of hydrochloric acid the modification, m.p. 184–185°, reappeared. The latter could again be converted to the 221–222° variety by 15-minute reflux in boiling water. The high melting variety decomposed completely when heated under vacuum at its melting point and did not yield any of compound XIV. The filtrate from the original acidified reaction system was found to yield at least 0.59 g of 1,4-↑↑-methylene-Δ^5-cyclohexene-2,3-↓↑-dicarboxylic acid, m.p. 187°. Treatment of the mercurial with concentrated hydrochloric acid also gave this product, authenticated by mixture melting point.

It was observed that the low melting 5-↑-hydroxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2-↓-3-↑-dicarboxylic acid at its melting point tended oftentimes to resolidify after melting. This property was utilized by heating 0.2 g, m.p. 184–185°, in a test tube under continuous water aspirator vacuum by immersion into a paraffin bath heated from 185° to 193° during 15 minutes. After cooling to 25° the residue was extracted with 10 ml of hot acetone. This extract was treated with commercial hexane to incipient turbidity. After several hours the system was filtered to remove a slight precipitate. Then the filtrate was vacuum-evaporated to leave a syrup which solidified when moistened with methanol. The solid product, 0.08 g (24%), melted at 232–232.5°, and was found by mixture melting point to be identical with 5-↓-hydroxy-6-↑-chloromercuri-1,4-↑↑-methylenecyclohexane-2-↑-3-↓-dicarboxylic acid, γ-lactone (m.p. 234°). The X-ray diffraction pattern also was identical with that of XIV.

5-↑-Hydroxy-1,4-↑↑-methylenecyclohexane-2-↓-3-↑-dicarboxylic Acid

A solution comprised of 129.6 g (0.3 mole) of 5-↑-hydroxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2-↓-3-↑-dicarboxylic acid in 480 ml (0.6 mole) of 5% aqueous sodium hydroxide was prepared during 2 hours of stirring. Then 442 g (0.66 atom Na) of 3.5% sodium amalgam was added with stirring during 2 hours, the temperature being maintained at 33°. Five hours later the system was filtered, chilled, strongly acidified by addition of 75 ml of concentrated hydrochloric acid, and continuously extracted with diethyl ether. The first 14-hour extract contained 7.9 g of unchanged mercurial as ether-insoluble material. Subsequently the extraction was continued for 40 hours longer.

The total extract (except for unchanged mercurial) was evaporated, dissolved in 200 ml of ethyl acetate, and then placed on a chromatographic column, 70 mm O.D. by 150 cm long of 100–170-mesh silica gel which had been deactivated by washing with U.S.P. chloroform. The column was first eluted with 4 liters of chloroform and the eluate was discarded. Likewise the first 2 liters of eluate were discarded after 2 liters of 1:1 chloroform – ethyl acetate (purified) and then pure ethyl acetate was used for elution. The next 1.5 liters yielded about 10 g of 1,4-↑↑-methylene-Δ^5-cyclohexene-2-↓-3-↑-dicarboxylic acid, m.p. 182–183°. The subsequent eluant (5 liters) yielded a semisolid upon evaporation which was crystallized from hot ethyl acetate to yield 55 g, m.p. 155–160° (90%). Recrystallization from ethyl acetate raised this melting point to 184.5°. The crystallization is accomplished by solution in 10–20 ml of solvent per gram after which 40% of the solvent is distilled off. The rate of crystal growth usually requires 4 to 5 days. Calc. for $C_9H_{12}O_5$: C, 54.1; H, 6.08. Found: C, 53.9; H, 6.04. The X-ray diffraction pattern was [10] 4.21, 5.05; [9] 5.79; [8] 5.60; [7] 3.44; [6] 3.26, 3.14; [5] 3.03; 3] 2.39; [2] 2.74; [1] 2.66, 3.91.

5-↓-Hydroxy-6-↓-chloromercuri-2-↓-carbomethoxy-1,4-↑↑-methylenecyclohexane-3-↓-carboxylic Acid, γ-Lactone (XXII, X = Cl)

A solution of 7.95 g (0.025 mole) of mercuric acetate in 80 ml of water was shaken with 5.25 g (0.025 mole) of molten dimethyl 1,4-↑↑-methylene-Δ^5-cyclohexene-2,3-↓↓-dicarboxylate (m.p. 37.5–38°) until the oil dissolved (8 minutes). Thirty minutes later the system was shaken vigorously while a solution of 1.5 g of sodium chloride in 5 ml of water was added slowly. The crude precipitate, methanol-washed and vacuum-dried, weighed 10.2 g, m.p. 201–203° (95%). This product was dissolved in 35 ml of dimethylformamide at 100°. The precipitate formed upon cooling weighed 6.45 g, m.p. 229–229.5° (60%). A methoxyl analysis showed 7.31% OCH_3, calc. 7.19%. The strongest lines of the X-ray diffraction pattern are [10] 9.30; [9] 4.61; [8] 3.61; [7] 2.92; [6] 5.81; [5] 6.55, 2.43; [4] 2.04. Recrystallization from dimethylformamide raised the melting point to 230.5–231°.

When this ester lactone (0.5 g) was dissolved in 1 ml of concentrated hydrochloric acid and the solution, after 12 hours, was diluted with water and let stand 1 week, crystals were obtained. The product, 0.115 g, m.p. 195–196°, was crystallized from hot water, m.p. 201°. A mixture melting point with 5-↓-hydroxy-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic acid, γ-lactone, was not lowered.

Saponification of the pure ester lactone was effected by maintaining a solution of 2.57 g (0.005 mole) in 18 ml (0.045 mole) of 10% aqueous sodium hydroxide for about 12 hours after which the system was boiled for $\frac{1}{2}$ hour. Acidification with 12% hydrochloric acid gave 1.96 g, m.p. 181°. Extraction with 40 ml of boiling water left 0.70 g, m.p. 219–220°, which was not lowered by admixture with XI. The cooled filtrate gave 0.68 g, m.p. 196–197°, from which successive crops of XI could be obtained. The final crop, 0.33 g, melted at 209–210° and was impure 5-↓-hydroxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2-↓-3-↑-dicarboxylic acid (XII) of X-ray diffraction pattern [10] 5.14; [8] 12.02; [7] 3.55, 3.94; [5] 3.07; [4] 4.30; [3] 4.47, 6.25; [2] 5.92, 6.73; [1] 10.84, 3.74.

A by-product was also found to be formed in the oxymercuration. When the dimethylformamide contained in the mother liquors from crystallization of the 10.2 g portion (above) was evaporated the residue upon quick crystallization from boiling water melted at 181°. After another quick crystallization it melted at 187–188° and resolidified to melt again at 214°. These properties identify it as 5-↑-hydroxy-6-↓-chloromercuri-1,4-methylenecyclohexane-2-↓-3-↑-dicarboxylic acid (XXIV). Further proof was obtained by heating 0.2 g under vacuum from 195 to 204° during 20 minutes. An acetone extract of the cooled residue, evaporated and treated with methanol, gave 0.05 g of 5-↓-hydroxy-6-↑-chloromercuri-1,4-methylenecyclohexane-2-↑-3-↓-dicarboxylic acid, γ-lactone (XIV), m.p. 232–233°, with partial X-ray diagram [10] 7.13; [9] 5.65; [7] 2.35; [6] 3.50; [5] 2.84; [4] 4.05.

Dimethyl 5-↑-Methoxy-6-↓-chloromercuri-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylate (XXIII, Z = Me, X = Cl)

To a solution of dimethyl 1,4-↑↑-methylene-Δ^5-cyclohexene-2,3-↓↓-dicarboxylate (1.05 g, 0.0047 mole) in anhydrous methanol containing 0.5 g (0.0035 mole) of boron fluoride etherate was added 1.58 g (0.005 mole) of mercuric acetate. After 4 minutes the salt dissolved, and after 10 minutes the whole was poured into 50 ml of 5% aqueous sodium chloride. After 2 days at 4° the precipitate was filtered, water-washed, and dried, 1.78 g, m.p. 97–121°. This mixture of acetoxy- and methoxy-mercurials was fractionally crystallized from ethyl acetate – isooctane solutions to give impure acetoxymercurial (X-ray diffraction pattern) and pure dimethyl chloromercurimethoxymethylenecyclohexanedicarboxylate, 0.5 g (10%), m.p. 130–131°. X-Ray diffraction pattern is [10] 6.96; [9] 3.97; [8] 5.34; [7] 3.42, 3.08; [6] 4.62; [5] 5.94, 4.27; [4] 2.91. A longer reaction time (36 hours) gave a lower weight yield (1.55 g) of higher (107–114°) melting point. Calc. for $C_{12}H_{17}ClHgO_5$: C, 30.2; H, 3.56; OCH_3, 19.5. Found: C, 30.4; H, 3.64; OCH_3, 19.1.

When XXIII was treated with concentrated hydrochloric acid, and after 1 hour, the system was evaporated to 20% of the original volume crystals of 5-↓-hydroxy-1,4-↑↑-methylenecyclohexane-2,3-↓↓-dicarboxylic acid, γ-lactone, appeared, m.p. 198°. Crystallization from water raised this melting point to 201–202° and a mixture melting point with an authentic sample was not lowered.

5-↑-Methoxy-1,4-↑↑-methylene-2,3-↑↑-[1′-↑-hydroxy-Δ^2-propene-1′,3′-ylene]-cyclohexane

A solution of 5-↑-methoxy-1,4-↑↑-methylene-2,3-↑↑-propenylenecyclohexane (prepared in 92% yield by use of sodamide rather than sodium (36)) in 200 ml of pure acetic anhydride was added dropwise to a stirred ice-cooled suspension of selenium dioxide (67.2 g, 0.6 mole) in 25 ml of water. Following then a comparable procedure (37), an acetate, b.p. 147° (12 mm), was obtained, n_D^{20} 1.4974, 87 g, 65%, % C, 71.0, % H, 8.40. Hydrolysis by the prescribed method gave an 83% yield of the methoxy alcohol, b.p. 148° (11 mm), n_D^{20} 1.5145. Calc. for $C_{11}H_{16}O_2$: C, 73.3; H, 8.88; Found: C, 73.8; H, 8.78.

5-↑-Methoxy-1,4-↑↑-methylene-2,3-↑↑-propenonylenecyclohexane

Following the recommended procedure (37) upon the methoxy alcohol described above an 83% yield was obtained, b.p. 147° (11 mm), n_D^{20} 1.5188, λ_{max} 225 mμ, E_{max} 8,650. Calc. for $C_{11}H_{14}O_2$: C, 74.1; H, 7.85. Found: C, 73.7; H, 7.70.

5-↑-Methoxy-1,4-↑↑-methylenecyclohexane-2,3-↑↑-dicarboxylic Acid

To a stirred solution of the unsaturated ketone (1.5 g) in 30 ml of acetone plus 1 ml of water was added 8 g of potassium permanganate during 10 minutes (37); the system boiled. After 2 hours of stirring 10 ml of water was added, followed by 20 ml of methanol. After 30 minutes the permanganate was reduced so the manganese dioxide was filtered off and washed with acetone and water. The residue from the vacuum-evaporated filtrate was dissolved in 10 ml of water and the solution acidified to pH 4 was saturated with sodium chloride and thoroughly extracted by ethyl ether. The extracts, evaporated, left 1.1 g of sticky solid which was crystallized from benzene–methanol and from water to give 0.68 g, m.p. 149–152°. Crystallization from methanol – ethyl acetate gave 0.37 g, m.p. 166–167°. Calc. for $C_{10}H_{14}O_5$: C, 56.0; H, 6.58. Found: C, 56.4; H, 6.73. X-Ray diffraction pattern is [10] 4.99; [9] 5.73; [8] 3.91; [7] 4.26; [6] 5.45.

Stability of Mercurials Toward Concentrated Hydrochloric Acid

After 1 year a suspension of 0.2 g of butylmercuric chloride in 2 ml of concentrated hydrochloric acid at room temperature was filtered to recover 0.19 g of the mercurial. The filtrate was evaporated to a volume of 1 ml and then was made basic with aqueous sodium hydroxide. No mercuric oxide was precipitated. The result was unaltered by inclusion of 0.01 g of mercurous chloride into the system.

A suspension of 0.1 g of cyclopentylmercuric chloride in 2 ml of concentrated hydrochloric acid and 1 ml of dioxane was refluxed for 1 day. The mercurial was all recovered unchanged, m.p. 112°. The inclusion of 0.01 g of mercuric chloride did not alter this result.

A mixture of 0.200 g each of β-2-chloromercuricineole and of phenylmercuric chloride in 2 ml of methanol was treated with 2 ml of concentrated hydrochloric acid. The system, which became warm, was cooled to room temperature and was stirred for 30 minutes. After dilution with water the solid phase was filtered off, 0.175 g, m.p. 255–256°, which was proved by mixture melting point to be phenylmercuric chloride. Addition of alkali to the filtrate gave 0.258 mmole of mercuric oxide.

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