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STEREOCHEMISTRY OF THE HYDROXY-MERCURATION OF ALKENES

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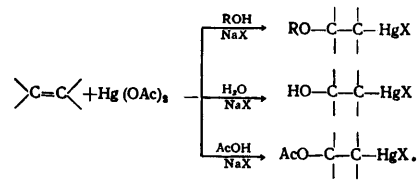
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I. INTRODUCTION

In 1892 Kucherov discovered that mercury(II) salts are capable of addition to a C–C double bond[1]. Eight years later — in 1900 — Hofman and Sand[2] developed this reaction, and in subsequent investigations it was shown that the reaction of alkenes with mercury(II) salts leads to the formation of hydroxyalkylmercury compounds and their derivatives:



Since then, hydroxymercuration has remained a subject widely studied from various viewpoints. Hydroxyalkylmercury compounds, being readily available, find application as pesticides, antiseptics, diuretics, preservatives, seed dressings, etc.

The alkoxyalkylmercury halide derivatives obtained in this way were used to solve several important theoretical problems. Thus the example of electrophilic substitution

by mercuric chloride on *cis*-2-methoxycyclohexylneophylmercury showed that the configuration is retained during bimolecular electrophilic substitution at a saturated carbon atom[3].

Hydroxymercuration can be applied to alkenes of various structures; it is simple to perform and usually takes place with high yields. Chatt[4] has reviewed the extensive literature on this reaction.

However, despite intensive study, the stereochemistry of hydroxymercuration has not yet been strictly established. On the one hand, the difficulty of determining the configuration of mercurated alcohols was due to the impossibility of using chemical methods, since in chemical reactions the C–Hg bond is affected and the reactions proceed with substitution at the asymmetric carbon atom, whereas the stereochemistry of electrophilic substitution at a saturated carbon atom has become known only in the last few years. On the other hand, the use of physical methods of investigation, for example, X-ray diffraction or the measurement of dipole moments, also did not allow the configuration of mercurated alcohols to be determined unambiguously and conclusively and in some instances led to incorrect conclusions. Thus in 1951 Brook and Wright[5] made an X-ray diffraction analysis of 2-methoxycyclohexylmercury chloride, obtained by the methoxymercuration of cyclohexene, and found that it has the *trans*-configuration. Because of this, in Chatt's review[4] the information on the hydroxymercuration was interpreted from the standpoint of *trans*--addition. However, in later studies[6-8] (see also Kreevoy and Kowitt[9]) Wright assumed error in the X-ray data and even expressed the opinion that this method is generally not very dependable when applied to the products of hydroxymercuration. [Now, however, the X-ray diffraction method is considered reliable (see IV, 2) (Ed. of Translation)].

The present review considers the stereochemistry of the hydroxymercuration of alkenes, which only recently has been established reliably, using various methods. It will be necessary to consider also some earlier work, already reviewed by Chatt[4]. Note that there is also a review by Wright[6] dealing with the hydroxymercuration of alkenes, but all its stereochemical conclusions are wrong.

II. MECHANISM OF THE REACTIONS OF HYDROXYMERCURATION AND DEHYDROXYMERCURATION

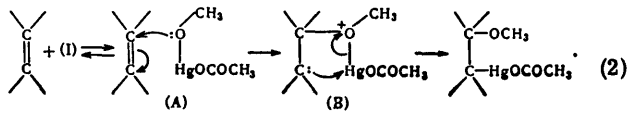
Because of the above-mentioned difficulties in establishing the configuration of mercurated alcohols attempts were made to determine it starting from the stereochemical requirements of the reaction mechanism.

The addition of mercury salts is electrophilic and the presence of electron-acceptor substituents hinders the reaction. Hydroxymercuration proceeds stereospecifically: from the *cis*- and *trans*-isomers of alkenes different diastereomers are obtained free from the second isomer as impurity; the reaction is not accompanied by *cis–trans* isomerisation of the alkene. The hydroxymercuration product of the *cis*-alkene is usually called the α-diastereomer; the β-diastereomer is formed from the *trans*-alkene, and also on isomerisation of the α-isomer. The dipole moment of the α-diastereomer is usually less than the β-diastereomer. The rate of hydroxymercuration of the *cis*-alkene is greater than that of the *trans*--alkene, which allows this reaction to be used to determine the configuration of the alkenes. Kinetic investigations showed that the reaction is second-order[6-8].

The mercurated alcohols are readily dehydroxymercurated, and because of this Nesmeyanov[10] called them "quasicomplex compounds". Dehydroxymercuration also proceeds stereospecifically and leads to the alkene of the original configuration, and many examples[11] have shown that the diastereomer with the lesser dipole moment is dehydroxymercurated more readily.

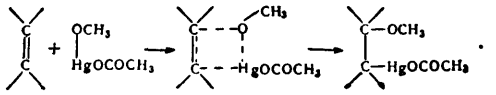
Two alternative mechanisms have been proposed for the hydroxymercuration. Wright[6,12,13] proposed a non-ionic mechanism in which there is first alcoholysis (hydrolysis) of the mercury(II) acetate with formation of a hydroxoacetatomercury(II) or an acetatoalkoxymercury(II) complex, which then reacts with the alkene in the slow stage of the reaction:

$$CH_3OH + Hg(CH_3COO)_2 \rightleftharpoons \underset{(I)}{CH_3OHgOCOCH_3} + CH_3COOH, \qquad (1)$$



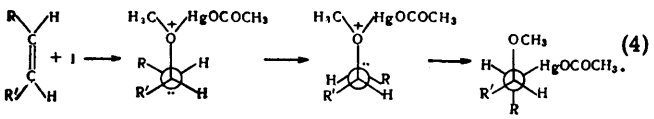
(2)

It is assumed that acetatomethoxymercury(II), (I), is in rapid equilibrium with mercury(II) acetate in methanol solution. Note that in the case when stages A and B are distinct this mechanism is inadmissible, since it presumes nucleophilic attack on the double bond by the methoxy oxygen. This difficulty is easily overcome by assuming that the slow stage of the reaction proceeds through a four-centred transition state:



(3)

In accordance with this reaction mechanism, hydroxymercuration should proceed as a *cis*-addition. Therefore in all of Wright's studies[6,7] the α-diastereomer is given the *cis*-configuration. The most substantial argument in support of the molecular mechanism is thought by Wright to be the fact that the rate of hydroxymercuration is greater in methanol than in water[7,14]. To explain possible instances of *trans*-addition, Wright introduced the "coordinative dipole" mechanism[14], according to which during the stage of the A → B change in scheme (2) there is rotation around the C–C bond:



(4)

This mechanism is undoubtedly incorrect, since the hydroxymercuration reaction is considered in essence again as a nucleophilic addition.

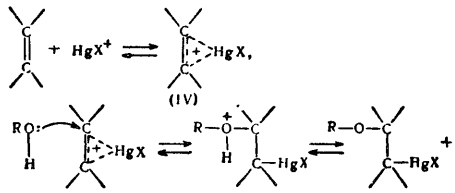
Winstein and coworkers[15] proposed an ionic mechanism on the basis of a study of the distribution of cyclohexene between carbon tetrachloride and water or an aqueous solution of mercury(II) nitrate; it was found that cyclohexene forms two types of complexes with the mercury ions, by schemes (5) and (6):

$$C_6H_{10} + Hg^{2+} \underset{}{\overset{K_1}{\rightleftarrows}} \underset{(II)}{C_6H_{10}Hg^{2+}}, \qquad (5)$$

$$C_6H_{10} + Hg^{2+} + H_2O \overset{K_2}{\rightleftarrows} \underset{(III)}{C_6H_{10}\overset{+}{H}gOH} + H^+, \qquad (6)$$

where $K_1 = 2.2 \times 10^4$ and $K_2 = 5.0 \times 10^4$.

The authors formulated the structure of these complexes by analogy with the "bromonium" cation [16] and expressed the opinion that similar complexes, especially singly-charged complexes of type (III), are intermediates in hydroxymercuration, which proceeds in this way by schemes (7)–(8):



(7)

(8)

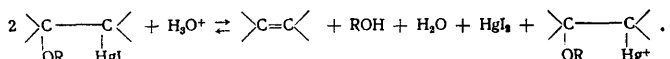
In accordance with this mechanism — by analogy with the discovery of other bridged ions which may be formulated as π complexes — hydroxymercuration should take place as a *trans*-addition.

Although subsequently Brook and Wright [17] found that under these conditions cyclohexene is converted into formylcyclopentane, this, however, does not disprove the results of Winstein and coworkers [15], since the rate of such a conversion is far less than the rate of reaching equilibrium in the distribution of cyclohexene between two phases (the measurements were made after 0.5, 1, and 1.5 h and were extrapolated to zero time).

One of the arguments put forward by Wright against an ionic mechanism [14] is the absence from the outer electron cloud of the mercury ion of free electron pairs by which a cyclic "onium" ion could be formed, analogous to that originally proposed, for example, for the bromine cation [16]. However, the cyclic ion proposed by Winstein and coworkers [15] must be considered essentially as a π complex [21] The electronic structure of the complex of the mercury ion with an alkene was considered by Dewar [18] (see also Kreevoy and Kowitt [9]), who proposed that in the alkenemercury(II) ion (IV) the $6sp$ hybrid orbital of the mercury atom overlaps with the two $2p$ orbitals of the carbon atoms, forming a pseudoaromatic structure. Here additional stabilisation is also possible with participation of the $5d$ electrons of the mercury and the antibonding π orbital of the alkene [9].

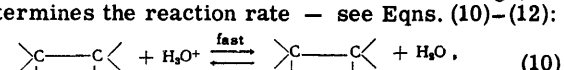
However, not one of the mechanisms of hydroxymercuration presented above explains certain features of this reaction; for example, catalysis by peroxides and by oxygen [11].

It seemed possible to draw reliable stereochemical conclusions only by studying the mechanism of dehydroxymercuration. Kreevoy showed [9,19–22] in 1959 that dehydroxymercuration by perchloric acid proceeds by the following stoichiometric equation:

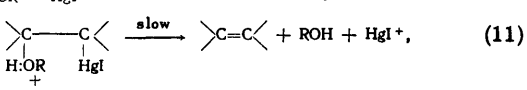


(9)

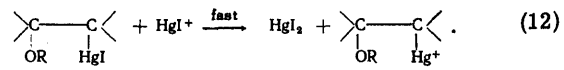
Detailed study of the mechanism of this reaction showed [9,19–22] that in the first stage there is a rapid and reversible addition of a proton to the alkoxy oxygen atom, with subsequent formation of alkene in the second stage, which determines the reaction rate — see Eqns. (10)–(12):



(10)



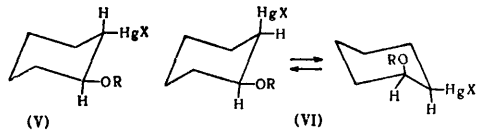
(11)



(12)

The reaction takes place very readily; for example, the rate of dehydroxymercuration of 2-hydroxypropylmercury(II) iodide is 10^{11} times as great as the acid-catalysed dehydration of propan-2-ol [9].

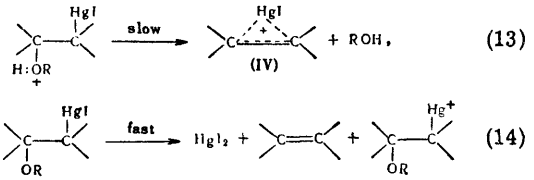
From the results of kinetic studies of the dehydroxymercuration of α- and β-2-methoxycyclohexylmercury(II) chloride, (Va) and (VIa) respectively, Kreevoy [9,21] drew convincing conclusions about the structure of the transition state at the stage which determines the rate of the reaction, Eqn. (11).



(a) R=CH$_3$; (b) R=H.

The α-diastereomer (Va) is dehydroxymercurated approximately 10^6 times faster than the β-diastereomer (VIa); for the α-diastereomer $\Delta H^{+} = 17.75 \pm 0.19$ kcal × × mole^{-1} and $\Delta S^{+} = 4.6 \pm 0.6$ cal mole^{-1} deg^{-1}, whereas for the β-diastereomer $\Delta H^{+} = 26.2 \pm 0.7$ kcal mole^{-1} and $\Delta S^{+} = 4.5 \pm 2.0$ cal mole^{-1} deg^{-1}.

Starting from these results for the rate-determining stage a structure was adopted for the mercurinium ion (IV) analogous to that proposed earlier [15]. Reactions (11) and (12) can be more strictly represented by Eqns. (13) and (14):

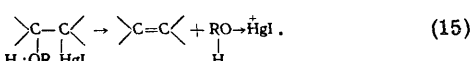


(13)

(14)

If the mercury and oxygen are in the *trans*-position, there will be a synchronous withdrawal of the ROH group and formation of the mercurinium ion, which proceeds without appreciable steric hindrance [9,21]. The required coplanarity of the groups being detached can be attained with little distortion of the bond angles only for the *trans*-isomer (in the diaxial conformation). Hence the dehydroxymercuration of the *trans*-isomer requires a lower activation enthalpy than the *cis*-isomer, and the α-diastereomer (Va) can be ascribed the *trans*-configuration. It is noteworthy that the activation entropies for the two diastereomers are similar. This shows that the solvation in the two transitional states is about the same.

The mechanism proposed by Wright can also be considered in its application to dehydroxymercuration where the rate-determining stage for the reaction is represented by the equation:



(15)

When, in accordance with Wright's results, the *cis*-configuration is taken for the α-diastereomer, then its higher rate of dehydroxymercuration should be due to the solvation of the mercury ion being detached by the methanol being better than that by water, which is generally improbable. Furthermore, the difference in the rates of dehydroxy-

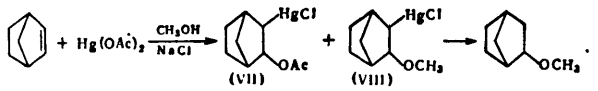
mercuration of two isomers should be due normally to differences in the entropies of activation rather than to the activation enthalpies[9].

Hence the information about dehydroxymercuration allows the *trans*-configuration to be fairly reliably ascribed to the α-diastereomer obtained by the hydroxymercuration of cyclohexene.

III. HYDROXYMERCURATION OF BICYCLOALKENES (IN THE ABSENCE OF PRELIMINARY COORDINATION OF THE MERCURY ION WITH THE SUBSTITUENTS)

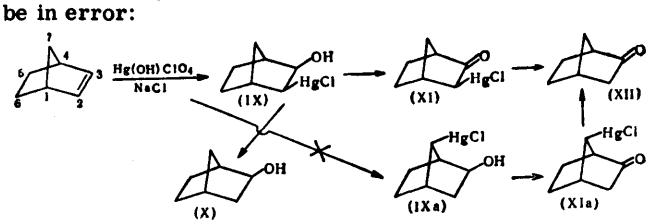
Of great interest in establishing the stereochemistry of hydroxymercuration is the study of this reaction in the case of bicyclo-bridged systems of the norbornene type. The geometry of these alkenes predetermines *exo*-attack of the reagent being added on, as was confirmed by an extremely large number of varied reactions[23-25]. On this basis the HgX group can be ascribed *exo*-configuration and then the problem of determining the stereochemistry of hydroxymercuration leads to the determination of the configuration of the hydroxy- or alkoxy-groups respectively.

In 1959 there appeared work by Wright and coworkers[7] and a brief communication by Traylor and Baker[26] devoted to the hydroxymercuration of norbornene. However, the stereochemistry of hydroxymercuration was interpreted differently in these papers. Wright and coworkers[7] found that under the action of mercury(II) acetate norbornene forms 3-acetoxynorborn-2-ylmercury(II) chloride (VII) or 3-methoxynorborn-2-ylmercury(II) chloride (VIII):



Unexpectedly, this reaction is essentially different in its stereochemical result from the hydroxymercuration of ordinary alkenes and undoubtedly takes place heterolytically, since it is catalysed by acids. The α-diastereomer formed is relatively stable to the action of acids whereas the β-diastereomer very easily undergoes dehydroxymercuration in acid; the dipole moment of the α-diastereomer is greater than that of the β-diastereomer. In the reduction of the α-diastereomer (VIII) methyl *endo*-norbornyl ether was obtained, and from this it was concluded that the α-diastereomer is the *trans*-isomer, additional confirmation of which was given by consideration of dipole moments. Since the stereochemistry of this reaction is the antithesis of what is observed for alkenes of the cyclohexene type, Wright considers that the hydroxymercuration of the latter should proceed as a *cis*-addition, that is, in accordance with the non-ionic mechanism.

Traylor and Baker[26] also concluded that the stereochemistry of the hydroxymercuration of norbornene is different from that observed for ordinary alkenes, but on reducing the α-diastereomer (IX) they obtained *exo*-norborneol (X) and therefore the alleged preparation of methyl *endo*-norbornyl ether in the above work[7] is considered to be in error:

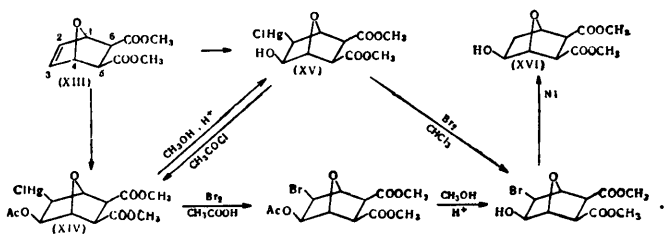


Hence the hydroxymercuration of norbornene proceeds as a *cis-exo*-addition, while the hydroxymercuration of ordinary alkenes takes place as a *trans*-addition through the intermediate mercurinium ion.

As is well known, ionic addition to norbornene can be accompanied by a Wagner–Meerwein rearrangement. This possibility was not considered by Wright and coworkers[7], whereas Traylor and Baker specially confirmed the absence of the rearrangement by oxidising the α-diastereomer (IX) to the ketone (XI) and reducing the latter with sodium stannite to norcamphor (XII), which is characteristic for the α-ketomercury chloride derivatives. However, this series of reactions is not a strict demonstration of the absence of rearrangement. The double bond of norbornene can participate in the stabilisation of the carbonium formed during the solvolysis of the 7-substituted derivatives[27,28]. Therefore the preparation of norcamphor can be explained starting from the structure of the *syn*-3-hydroxynorborn-*exo*-7-ylmercury(II) chloride for the α-diastereomer (IXa), assuming the interaction of the 2-keto- and 7-chloromercury-groups in the ketone (XIa) on reduction.

The stereochemical data on the hydroxymercuration of norbornene were supplemented by Yur'ev and coworkers[29-31] in a study of the hydroxymercuration of a similarly constructed bicyclo-system — 7-oxanorbornane, having an oxygen bridge atom, for which the correctness of the *exo*-addition rule had been shown earlier[32]. In order to avoid the Wagner–Meerwein rearrangement, the model selected for studying the stereochemistry of hydroxymercuration was the dimethyl ester of *exo-cis*-7-oxanorborn-2-en-5,6-dicarboxylic acid (XIII). The presence of electron-acceptor groups in this type of bicyclo-compound greatly reduces the rate of solvolysis of halides[33], stabilises the α-oxide ring[34] and results in most of the additions at the double bond proceeding without the Wagner–Meerwein rearrangement[35,36], although in principle all courses of the reaction with rearrangement are possible also in the presence of electron-acceptor groups[35,36].

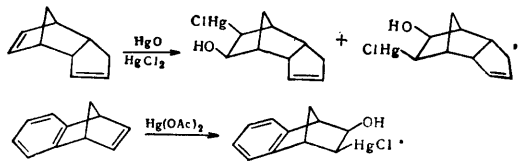
Hydroxymercuration of the diester (XIII) leads to the acetoxy- (XIV) or hydroxy-derivative (XV), depending on the conditions[31]:



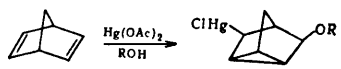
The compounds obtained, like *exo-cis*-3-hydroxynorborn-2-ylmercury chloride (IX), seemed relatively stable in acid. The *exo*-hydroxydiester (XVI) was obtained by a series of successive conversions from (XIV) and (XV), the configuration of which had been established earlier[31,32]. Hence the hydroxymercuration of the diester (XIII) proceeds by an *exo-cis*-addition (additional proofs are given below).

In 1963 Traylor and Baker showed that the hydroxymercuration of bicyclopentadiene and benznorbornene takes

place as an *exo-cis*-addition without the Wagner–Meerwein rearrangement[37]:



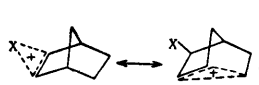
It is interesting that norbornadiene reacts with mercury(II) salts as a homoallyl system with participation of the two double bonds and formation of a 6-acetoxy- or 6-alkoxy-tricyclo[2,2,1,$0^{3,5}$]hept-2-ylmercury(II) chloride[38,39]:



From the above information on the study of hydroxymercuration there is no doubt that stereochemically the course of this reaction depends on the type of alkene taking part: in unsaturated bicyclo-systems having sterically hindered *endo*-attack, hydroxymercuration proceeds as a *cis*-addition, whereas the hydroxymercuration of ordinary alkenes of the stilbene or cyclohexene type takes place as *trans*-addition.

It must be emphasised, however, that the problem of the reason for *cis*-addition in hydroxymercuration is not completely clear. The opinion has already been expressed in the literature that strongly solvated bridged onium ions or π complexes can, in the case of hindrance to *trans*-attack by a nucleophilic agent, undergo *cis*-opening of the ring as revealed by the products[26,31,37]. This finds confirmation in the stereochemistry of additions or rearrangements taking place through an intermediate π complex of a proton with the alkene, or a bridged "protonium" ion. The disclosure of such an undoubtedly strongly solvated ion proceeds anomalously stereochemically in comparison with the usual *trans*-opening of intermediate cyclic onium ions (or π complexes), as has been shown by several examples[40,41]. Similar behaviour can occur during hydroxymercuration. Confirmation of this is obviously provided by the fact that the action of mercury(II) acetate in methanol on norbornene gives a mixture of 3-acetoxynorborn-2-ylmercury chloride (VII) and 2-methoxynorborn-2-ylmercury chloride (VIII).[7] In the case of *trans*-addition the methanol concentration is immeasurably greater than that of the acetate anion, and the reaction leads almost solely to the formation of the methoxy-derivative. In the case of *cis*-addition, the anion which attacks the intermediate mercurinium ion is taken from the solvate sheath of the mercury ion.

However, the hindrance to *trans*-opening of the mercurinium ion obviously cannot be explained solely by the steric shielding of the double bond from the *endo*-side. It was noted[37] that in bicyclo-systems it is difficult to attain a planar transition state for *trans*-addition. However, examples of *trans*-opening of an α-oxide ring[32,32] or of *trans*-addition at the double bond[36] nevertheless show the possibility in principle of such a transition state. Yet another factor is probably required in explaining the cases of *cis*-hydroxymercuration in bicyclo-systems, namely, the contribution in the transition state of a structure with partial delocalisation of the electrons of the 1,6- and 4,5-bonds:



An analogous explanation was postulated for instances of radical *cis*-bromination[43], but it can probably be applied also to heterolytic processes. The contribution of this type of structure was also introduced to explain some instances of *endo-exo*-isomerisation[44].

It has also been suggested that *cis*-hydroxymercuration is due to the directional effect of the double bond in the bicyclo-systems studied[37]. If this is really so, then the hydroxymercuration of strained monocyclic alkenes of the cyclobutene and cyclooctene type should also proceed as a *cis*-addition.

IV. METHODS OF FINDING THE CONFIGURATION OF 2-MERCURATED ALCOHOLS

1. Nuclear Magnetic Resonance

In 1961 Anderson and Henry[45] used nuclear magnetic resonance to find the configuration of the α-diastereomers obtained by hydroxymercuration of norbornene (IX) and cyclohexene (Vb). In the nuclear magnetic resonance spectrum for (IX) the coupling constant between protons 2 and 3, J_{23}, is 6.8 Hz, which agrees closely with the constant found for the *endo-cis*-hydrogen atoms (7.7 Hz) and is greatly different from that found for *trans*-hydrogen atoms (2.2 Hz). Hence (IX) has an *exo-cis*-configuration.

It was found for (Vb) that the hydrogen atom at the carbon attached to the mercury has two coupling constants, equal to 10 Hz and characteristic for axial–axial coupling, and also one constant, equal to 3.5 Hz, characteristic for axial–equatorial coupling. Hence the mercury atom and the hydroxyl group should be in the equatorial position and (Vb) should have *trans*-configuration.

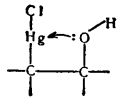
2. X-Ray Diffraction

As mentioned above, Brook and Wright ascribed the *trans*-configuration to α-2-methoxycyclohexylmercury(II) chloride (Va) and the *cis*-configuration to the β-isomer (VIa) on the basis of X-ray diffraction studies. Later, Wright suggested that these results are questionable and unreliable[6–8] (see also Kreevoy and Kowitt[9]). However, as has now been established, the configurations deduced from the X-ray diffraction studies are correct. Obviously doubt about the possibilities of applying this method to organomercury compounds are greatly exaggerated and Brook and Wright's original data[5] are reliable.

3. Infrared Spectroscopy

Traylor and Baker[37] developed a method of determining configuration by comparison of the infrared spectra of hydroxymercuration products and the corresponding hydroxy-compounds in the region of the stretching vibrations of the hydroxyl group. In this region in the infrared spectrum of 2-mercurated alcohols there is only one absorption band, which shows the absence of a hydrogen bond between the hydroxyl group and the mercury atom. In the *cis*-compounds there is a single additional interaction,

absent from *trans*-compounds, namely the interaction of the oxygen of the hydroxyl group with the mercury atom:



Owing to this, displacement of the absorption band of the hydroxyl group into the long-wave region should be greater in the case of *cis*-compounds. Experimental investigation showed that the displacement of the hydroxyl group band in *trans*-hydroxymercury(II) chloride derivatives, as compared with the corresponding hydroxy-derivatives is 6–10 cm^{-1}, whereas that for the *cis*-hydroxymercury(II) chloride derivatives is 18–22 cm^{-1}. However, this method should obviously be used with caution for compounds exhibiting free rotation of a C–C bond or conformational mobility of the ring.

4. Dipole Moments

Dipole moments were measured for several pairs of diastereomeric 2-mercurated alcohols[7,11]. Although the measurement of dipole moments is one of the principal methods for establishing the configuration, this method has led to incorrect conclusions in a series of hydroxymercurated alcohols[7]. Only a qualitative correlation has been noted between the rate of dehydroxymercuration and the magnitude of the dipole moment: the diastereomer with the lower dipole moment is more readily dehydroxymercurated in acid[11].

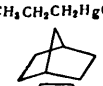
The main difficulty in using dipole moments is, according to Wright[7], the uncertainty in the C–Hg–X angle. On considering the vector scheme of the moments of the C–Hg–Cl group, Wright found that the angle between the moments of the C–Hg and Hg–Cl bonds is acute and amounts to 80°. Hence assuming free rotation, it turns out that the resultant vector moment of the C–Hg–Cl group (3.66 D) precesses 59° relative to the C–Hg bond and in the opposite direction. In this context, the calculations are very difficult, since there are two non-regular functional groups in the molecules of the 2-mercurated alcohols. Therefore, depending on the conformation, the dipole moment can change strongly and the choice of preferential conformations for the given compounds is arbitrary.

We have calculated the dipole moments of some 2-mercurated alcohols and found that dipole moments can be used to determine configuration but the angle C–Hg–X should be taken as 180°. Actually, investigation of the vibrational spectra and electron diffraction studies showed[46] that $HgCl_2$, $HgBr_2$, HgI_2, HgBrCl, HgICl, and HgIBr molecules are linear, while in the X-ray diffraction studies[5] mentioned above it was found that the angle C–Hg–X is 180° and 178° for (Va) and (VIa) respectively. Hence the C–Hg–X group can be considered linear, which greatly facilitates the calculation, since it is not necessary to consider the moment of the Hg–X bond separately and the whole moment of the HgX group can be considered directed along the C–Hg bond. The value of the moment along the C–HgCl bond can be taken as approximately equal to the dipole moment of propylmercury(II) chloride (3.70 D in dioxan).

The moment of the methoxy-group was taken as 1.30 D, with 55° as the angle of precession relative to the bond direction[47]. We made the calculation on the assumption that there is free rotation of the methoxy-group; the total moment was calculated as the mean of four moments: from the maximal and minimal values of coordinate z and two extreme values with coordinate $z = \frac{1}{2}(z_{max} + z_{min})$ for the vector of the methoxy-group. The vectorial scheme of the norbornane molecule was taken from Wilcox[48]. The Table gives the dipole moments which we have calculated on this basis and shows that the agreement between the experimental and calculated values is good (except for compound 7) despite several assumptions having been made in the calculation: the interaction between the oxygen atom and the mercury atom in *cis*-compounds has been neglected, and the mean moment of the C–Hg–Cl bonds is unknown and can only approximately be taken as equal to the moment of propylmercury(II) chloride. An unfavourable circumstance is that the dipole moments were measured in dioxan, which can be coordinated differently with the mercury atoms in different isomers. The discrepancy between the found and calculated dipole moments for compound 7 is to be expected, since in the *endo*-derivatives of norbornane there is considerable steric interaction, leading to distorted geometry of the molecule.

Qualitatively, the similarity between the experimental and calculated values is completely adequate for unambiguously establishing the configuration. In rigid cyclic systems in the absence of other groups which exhibit their own substantial dipole moment and in the presence of rotation of the methoxy-group the moment of the *cis*-isomer will be greater than that of the *trans*-isomer, since the moments of the methoxy and chloromercury(II) groups in the *cis*-compound are directed to one side, and in the *trans*-compound the moments of these groups are directed at an obtuse angle. Hence it is also understandable that if in accordance with Wright's results it is assumed that the moment of the –HgCl group is directed to the opposite side with respect to the C–Hg bond at an angle of 59°, then we obtain on calculating in the reverse order of the calculated quantities the value of the dipole moments for the *cis*- and *trans*-isomers.

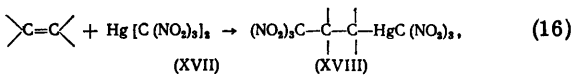
TABLE. Dipole moments of the derivatives of 2-mercurated alcohols.

Compound No.	Formula	Dipole moment, D		Δμ	Reference
		found	calculated		
1	$CH_3CH_2CH_2HgCl$	3.70			7
2		0.45			7
3		4.1	4.38	−0.28	11
4		2.9	3.38	−0.48	11
5		4.22	4.24	−0.02	7
6			3.22		
7		2.77	3.80	−1.03	7

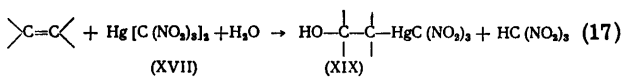
5. Methods Based on Difference in Dehydroxymercuration Rates

As already indicated above, the rate of dehydroxymercuration for the *trans*-isomer is much greater than that for the *cis*-isomer. Therefore on the basis of the measurement of the kinetics of dehydroxymercuration, configurations can be ascribed to pairs of diastereomeric 2-mercurated alcohols and this has been done [9,20,21]. Manolopoulos and coworkers [49] developed a relatively simple semiquantitative method for comparing dehydroxymercuration rates. The inconvenience of this method is that for a strict proof it is necessary to have the β-diastereomer, which is not always available.

A method of determining the stereochemistry of the addition of mercury salts with the aid of bis(trinitromethyl)mercury(II) (XVII), based essentially on the same principle, was developed by Zefirov and coworkers [50]. This compound is able to add on to alkenes to form derivatives of trinitromethyl-3,3,3-trinitropropylmercury(II) (XVIII) [51-53]:



(16)

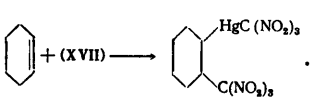


(17)

On carrying out the reactions in water it could be expected that Eqn. (17) would hold, with the formation of derivatives of 2-hydroxyethyltrinitromethylmercury(II) (XIX). However, the formation under such conditions of compounds of type (XIX) is possible only in the case of their stability in acid, since the trinitromethane liberated is itself a relatively strong acid ($K = 6.8 \times 10^{-1}$) [54]. Derivatives of type (XVIII) obtained by Eqn. (16), are extremely stable in acid [53], since their demercuration must be accompanied by rupture of a C–C bond. The stereochemical course of the reaction of hydroxymercuration according to Eqn. (17) should be the same for any mercury salts, especially if the possibility of the intermediate formation of a doubly-charged mercuronium ion of type (II) is taken into account — Eqn. (5).

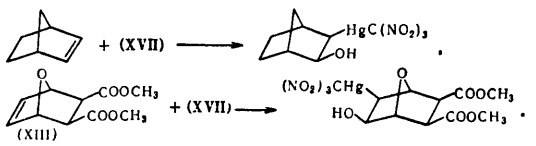
Hence, to determine the stereochemistry of the addition of mercury salts to an alkene the reaction must be carried out with an aqueous solution of bis(trinitromethyl)mercury(II), so that the formation of an addition product of type (XVIII) will show that the hydroxymercuration of this alkene proceeds as a *trans*-addition, whereas the formation of a product of type (XIX) will show *cis*-addition. Compounds of types (XVIII) and (XIX) are easily distinguished in the product analyses.

Actually, the addition of (XVII) to cyclohexene always proceeds with formation of trinitromethyl-2-trinitromethylcyclohexylmercury(II), whatever the solvent [52]:



The configuration of derivatives of type (XVIII) which are obtained has not been established experimentally, but probably *trans*-addition takes place here.

However, norbornene and the dimethyl ester (XIII) react with an aqueous solution of bis(trinitromethyl)mercury(II) according to Eqn. (17), [50] that is, *cis*-addition occurs here:



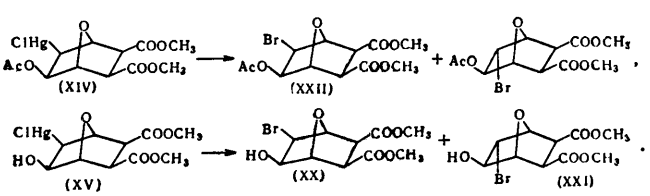
These methods are inapplicable when the stability of the 2-mercurated alcohol is due to some other structural factor. One of such factors is intramolecular closing of lactone rings, and also of tetrahydrofuran or tetrahydropyran rings [52-53].

6. Method of Replacement of HgX Groups

In connection with progress in investigations of the mechanism and stereochemistry of electrophilic substitution at a saturated carbon atom [55,56] it became possible to use chemical methods to determine the configuration of 2-mercurated alcohols. The replacement of halogenomercury-groups by halogen is the most convenient for this purpose, since the configuration of the halogenoalcohols obtained is usually known already or is relatively easily established by the usual methods. The stereochemistry of electrophilic replacement of chloromercury-groups by bromine was first studied by Jensen and Gale [57] who found that in non-polar solvents bromination takes place by a homolytic mechanism with racemisation or partial retention of configuration; bromination in polar solvents, for example, acetic acid, proceeds mainly with retention of the configuration. During bromination in pyridine there is complete retention of the configuration (S_E2 reaction), but the yield of the corresponding halogeno-derivative is only 50–65%, due to resinification taking place. Later, these conclusions were refined and supplemented (see Uglova [58]).

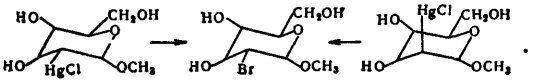
It must be emphasised that there has been no systematic study of the stereochemistry of electrophilic replacement of the HgCl group by halogen in the presence of neighbouring substituents.

Yur'ev and coworkers [31] used the halogenation of 2-mercurated alcohols with replacement of the HgX group as a method of finding configuration; they took as examples *exo*-3-acetoxy-5,6-dimethoxycarbonyl-*endo*-7-oxanorborn--2-ylmercury chloride (XIV) and *exo*-3-hydroxy-5,6-dimethoxycarbonyl-*endo*-7-oxanorborn-2-ylmercury chloride (XV).



It was found that bromination of the hydroxyester (XV) in chloroform leads to the *cis*-bromo-alcohol (XX) mixed with a little of the *trans*-bromo-alcohol (XXI), whereas bromination in pyridine leads only to the *cis*-bromo--alcohol (XX). The bromination of the acetoxyester (XIV) is analogous.

However, Jensen's rule about the retention of the configuration during bromination of organomercury compounds in polar solvents must be applied with caution to 2-mercurated alcohols, since it is possible that the presence of neighbouring substituents can alter the stereochemical result of the reaction. Inversion of the configuration during halogenation in several 2-mercurated alcohols was shown by the example of the bromination of the hydroxymercurated product of D-glucal[49], where both diastereomers gave identical bromomethoxy-derivatives:



Unfortunately, in this work the stereochemistry of bromination was investigated only in methanol and in carbon tetrachloride. Apparently, in the latter solvent reactions can also proceed by a radical, instead of S_E2 mechanism and in view of the considerable importance of the question, a study of the stereochemistry of bromination of these compounds in acetic acid and especially in pyridine would be welcome. Furthermore, a paper by Inglis and Schwarz appeared simultaneously[59] in which the hydroxymercuration of D-glucal and its triacetate is considered as *trans*-addition, and hence the results of these two studies are incompatible.

It should also be noted that in finding the configuration of 2-mercurated alcohols by other methods they can act as a convenient model for studying the stereochemistry of electrophilic replacement at a saturated carbon atom.

7. Method of Calculating the Angle of Rotation of Optically Active 2-Mercurated Alcohols

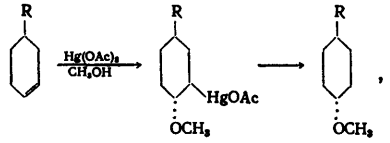
In 1963 Sokolov and Reutov[60] calculated the molecular rotation for certain optically acitive organomercury compounds by Brewster's method and showed that this type of calculation can be used to show the stereochemistry of the addition of mercury salts to alkenes. In 1947 Romeyn and Wright[61] obtained optically active α- and β-2-methoxycyclohexylmercury chloride (Va) and (VIa), with $[M]_D$ = = -139° and +45° respectively, by an asymmetric synthesis. The molecular rotation calculated[60] for the *trans*-isomer (Va) is -130° and hence the α-diastereomer should have the *trans*-configuration.

The use of this method is restricted by the difficulty of obtaining optically 2-mercurated alcohols of high purity. Naturally, calculation of the molecular rotation of organomercury compounds is restricted to those models for which Brewster's method is generally applicable[62].

V. HYDROXYMERCURATION OF ALKENES WHEN THERE IS PRELIMINARY COORDINATION OF A MERCURY ION WITH FUNCTIONAL GROUPS

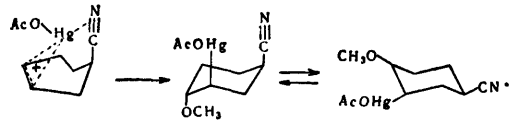
Due to the strong tendency of mercury to form coordination bonds, its preliminary reaction with functional groups attached to the alkene is possible in principle. Depending on the position of the functional group in relation to the reaction centre, such coordination can determine the direction of the initial attack of the mercury ion on the double bond, and consequently can lead to stereochemically anomalous reaction products.

In 1959 Henbest and Nicholls[63] hydroxymercurated 4-substituted cyclohexenes and in subsequent reduction obtained the corresponding *trans*-derivatives:

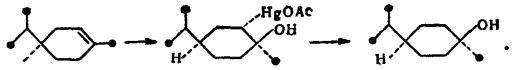


where R = OH, OCH_3, CH_2OCH_3, $COOCH_3$, CN.

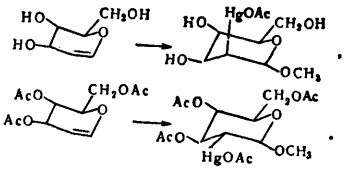
Hence assuming that the hydroxymercuration takes place as a *trans*-addition it follows that the atom of mercury atom is initially coordinated with the substituent and this determines the stereochemical course of the addition in a given case:



In the absence of preliminary coordination the *cis*-derivative is obtained after reduction, as the example of carvomenthene showed[64]:

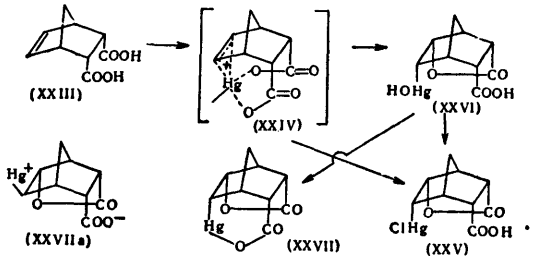


Manolopoulos and coworkers[49] found further that hydroxymercuration of D-glucal takes place as a *cis*-addition, whereas its triacetate is hydroxymercurate with formation of a *trans*-addition product:



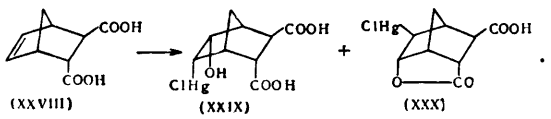
Such a difference in the stereochemical course of hydroxymercuration was explained by the preliminary coordination of the mercury ion with the hydroxyl groups in D-glucal. We must remember, however, that according to the results of Inglis and Schwarz[59] hydroxymercuration of glucal is a *trans*-addition[59], and therefore these studies need experimental verification.

The problems of the stereochemistry of hydroxymercuration when there is preliminary coordination were studied in considerable detail by Wright and coworkers[7,65], using norbornene derivatives with *endo*-functional groups. Thus the hydroxymercuration of the *endo*-norbornene-dicarboxylic acid (XXIII) proceeds as an *endo-cis*-addition to form the lactone (XXV)[7,65]:



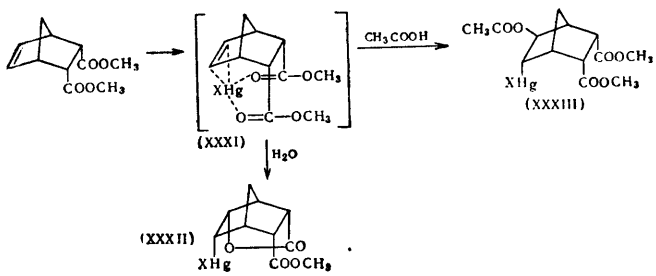
This stereochemical course of the reaction is thought by the authors to be brought about by the preliminary formation of the complex (XXIV). The *endo*-configuration of the HgCl group was demonstrated by obtaining the anhydrolactone (XXVII) by the action of acetic anhydride on the lactonemercury hydroxide (XXVI).

Hydroxymercuration of the *trans*-acid (XXVIII) proceeds less stereospecifically and leads to a mixture of the products of *endo-cis*- (XXIX) and *trans*-addition (XXX)[7]:



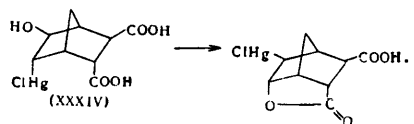
(XXVIII) (XXIX) (XXX)

Preliminary coordination of the mercury ion can also be effected with the methoxycarbonyl groups. Hydroxymercuration of dimethyl *endo-cis*-norbornenedicarboxylate proceeds in different directions with different solvents[7]. The coordination complex formed in the first stage (XXXI) gives the *endo*-lactonemercury chloride (XXXII) in water. In acetic acid, there is *trans*-opening with formation of the diestermercury chloride (XXXIII):



(XXXI) (XXXII) (XXXIII)

However, this paper[7] describes a series of conversions which raise doubts about the correctness of the allotted configurations. Thus, the thermal conversion of the *exo*-hydroxy-acid (XXXIV) into the lactone (XXX) remains uncertain:



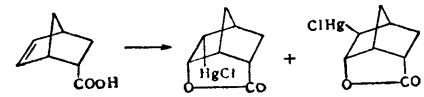
(XXXIV) (XXX)

[Carried out in sodium amalgan (Ed. of Translation)].

The dipole moments measured for many of these substances[7] are not reliable criteria for finding the configurations of such polyfunctional compounds. Essentially *endo-cis*-addition was only shown by the formation of the anhydrolactone (XXVII). The reliability of such a method is subject to doubt[9] and it was suggested that this compound exists in the form of a "zwitter-ion" (XXVIIa) with the mercury atom in the *exo*-position. Compounds existing in the form of "zwitter-ions" were obtained earlier in the hydroxymercuration of certain unsaturated acids[66]. Unfortunately Abercrombie and coworkers[7] did not measure the dipole moment of the anhydrolactone (XXVII).

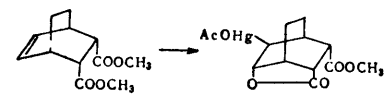
If the anhydro-compounds actually exist as "zwitter-ions" then all the data on the stereochemistry of the hydroxymercuration of norbornene derivatives having *endo*-functional groups, and for which initial *endo*-attack of the double bond by the mercury ion is assumed, due to preliminary coordination of the latter with the *endo*-substituent, must be reconsidered, and the question of the possibility of an anomalous stereochemical course of reaction remains open.

Malaiyandi and Wright[67], in studying the hydroxymercuration of *endo*-norbornenecarboxylic acid, separated two compounds which were given the following configurations:

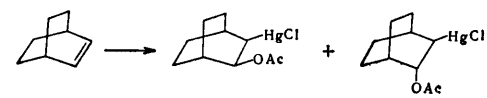


However, in this work the proof of the configuration is not strict — it is based on the analogy between the dipole moments with those of the already available products of the hydroxymercuration of norbornenedicarboxylic acids.

An ester of a bicyclooctenedicarboxylic acid was also first assumed to undergo *endo-cis*-addition[65] but it was found subsequently that *trans*-addition takes place[68]:

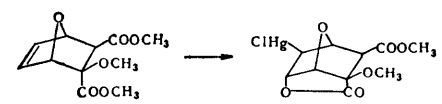


However, according to Traylor's later results[69] hydroxymercuration of bicyclooctene proceeds with formation of a mixture of the products of *cis*- and *trans*-addition:



It is therefore possible that the products of *cis*-addition to the dimethyl bicyclooctenedicarboxylate could not be separated because of experimental difficulties.

Yur'ev and coworkers[70] have shown that the hydroxymercuration of dimethyl 5-methoxy-7-oxanorborn-2-en-*trans*-5,6-dicarboxylate also proceeds by *trans*-addition:



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The most general features of the principal stereochemical rules for the addition of mercury(II) salts to alkenes have now been explained. It has been found that unlike other reactions of electrophilic addition at multiple bonds the stereochemical course of this reaction depends strongly on the alkene: the hydroxymercuration of ordinary acyclic and monocyclic alkenes is a *trans*-addition, whereas the hydroxymercuration of unsaturated, strained bridge bicyclo-compounds, having spatial hindrance against *trans*-attack, is a *cis*-addition.

However, there are many problems still awaiting solution. Thus the details of the mechanism of this reaction are still not clear, and the question of the possibility of anomalous stereochemical course of reaction due to preliminary coordination with functional groups has still not been decided unambiguously.

Undoubtedly, further investigation will lead to progress in understanding the fine stereochemical aspects of this reaction and may allow the rules found to be applied to a wider range of other additions.

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