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Abstract

Full Text

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CALCULATION OF THE ROTATION OF OPTICALLY ACTIVE ORGANOMERCURY COMPOUNDS AND THE STEREOCHEMISTRY OF THE ADDITION OF MERCURY SALTS TO OLEFINS

The theoretical calculation of the magnitude of the rotation of optically active compounds is one of the most important problems of stereochemistry, approaches to the solution of which until recently were extremely difficult. In 1959 J. Brewster ([1]) published a method for calculating the molecular rotation of compounds whose optical activity is due to an asymmetric carbon atom. It is based on the idea of a connection between the magnitude and sign of the rotation of the plane of polarization and the polarizability of atoms bound to the asymmetric center. A very important element of the theory is the development of the concept of conformational asymmetry for compounds with free rotation about single bonds. This made it possible to take into account the contribution made by atoms remote from the asymmetric center. The contribution of a structural unit of 4 atoms in the depicted conformation is expressed by the following quantity, calculated from the values of the atomic refraction of the terminal atoms:

$$\Delta[M]_{XY} = +k(X-H)(Y-H) = +160\left(R_X^{1/2} - R_H^{1/2}\right)\left(R_Y^{1/2} - R_H^{1/2}\right).$$

In the present work we describe the results of applying Brewster' s method to the calculation of the rotation of a few known optically active compounds whose molecules contain a mercury atom at the asymmetric carbon. The magnitude of the atomic refraction of mercury was calculated* from the values of the refractive index and the specific gravity for several representatives of the dialkylmercury series and was found to be equal to 12.80 cm^3, in agreement with the literature data. From the formula given above we obtain

$$\Delta[M]_{\mathrm{HCg}} = k(\mathrm{Hg}-\mathrm{H})(\mathrm{C}-\mathrm{H}) = 246^\circ.$$

Fig. 1

Fig. 1

Figure 1: Fig. 1

Let us present the calculation of the molecular rotation for 2-bromomercuributane. We construct the Newman projection along the C_2—C_3 bond, with the asymmetric atom in front. Figure 1 shows three possible conformations of the L-antipode (absolute configuration R). Of these, conformation A is forbidden because of maximum eclipsing; the contribution of conformation B is equal to $-k$(Hg—H)(C—H), and that of V to $+k$(C—H)^2. It is not difficult to see that these three variants exhaust the

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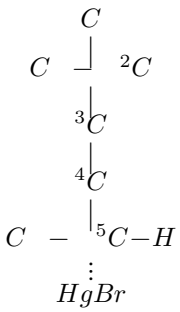
* The refractions of the other atoms were taken from the work of Vogel ([2]).

in this case all possibilities. Consequently, the molecular rotation of the L-form is

$$[M]_D = \frac{k(C-H)^2 - k(C-H)(Hg-H)}{2} = \frac{60-246}{2} = -93^\circ.$$

The greatest specific rotation of 2-bromomercuributane was obtained by Jensen ([3,4]): -25.8°, which corresponds to a molecular rotation of -87°, but the authors considered that the maximum rotation had not yet been attained.*

The second organomercury compound resolved into antipodes is 2-methyl-5-bromomercurihexane, whose L-antipode is shown in Fischer projection



It should have the same rotation if the $HgBr$ group is equal to methyl in volume ([1]). The minus sign is for the L-configuration (absolute–R), the plus sign for the D-configuration. The experimental molecular rotation is ([5]) 155.5°.

The successful application of Brewster's method to the calculation of the optical rotation of organomercury compounds led us to the idea of using this method to elucidate the stereochemistry of the addition of mercury salts to olefins, using cyclohexene as an example.

chemical structures of compounds I and II with rotations

Figure 2: chemical structures of compounds I and II with rotations

The reaction of addition of mercury salts to a double bond has been known for more than 60 years, but in the literature there is no generally accepted opinion concerning its mechanism and, in particular, its stereochemistry; both the forward reaction and the reverse reaction—deoxymercuration—proceed stereospecifically. Lucas, Hepner, and Winstein ([6]) proposed the theory of the mercurinium ion (by analogy with the bromonium ion), which assumed trans addition. Wright ([7]) advanced a "molecular" mechanism: an intermediate basic mercury salt is formed, which then adds to the double bond. A special role in the study of stereochemistry was played by addition to cyclohexene, owing to its geometrical simplicity and the absence of a second olefin isomer. In 1951 Brook and Wright ([8]), on the basis of X-ray structural analysis, concluded that the α-isomer of 2-methoxy-1-chloromercuricyclohexane (I), obtained by direct addition of mercury acetate in methanol to cyclohexene, has a trans configuration, while the β-isomer (II), formed upon isomerization of I by free radicals, has a cis configuration. Subsequently it was found that norbornene-5,6-dicarboxylic acid and its esters add mercury salts in the endo-cis position ([9]). The concept of a "molecular" mechanism for oxy- and deoxymercuration, and the discovery of the unreliability of the X-ray structural data for isomers I and II ([10,11]), led Wright to accept the cis configuration for adducts from cyclohexene and other simple olefins. Other investigators, especially Kreevoy, who studied the kinetics of deoxymercuration, adhere to the concept of the mercurinium ion and the trans configuration of the adducts ([12–14]). The reaction with a bicyclic olefin —norbornene—has a number of special features and, possibly, follows another mechanism. Opposite configurations were simultaneously assigned to the norbornene adduct with mercury acetate: trans by Wright ([15]), and cis by Traylor ([16]).

We calculated, by Brewster's method, the molecular rotation of the cis and trans isomers of 2-methoxy-1-chloromercuricyclohexane and compared them with the experi-

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* Jensen had already noted the agreement of the sign determined by Brewster' s rules with that found for the *L*-antipode, but did not give a quantitative calculation ([3]).

fundamental. Optically active I and II were obtained in 1947 by Romain and Wright (17), by adding mercury L-lactate to cyclohexene

The trans compound must have conformation ee, at least predominantly, and the molecular rotation $[M] = -k(\mathrm{Hg—H})(\mathrm{O_{ef}—H})$

The minus sign corresponds to the D antipode shown in the scheme (absolute

Newman projection

Figure 3: Newman projection

Newman projections of cis isomer conformers

Figure 4: Newman projections of cis isomer conformers

configuration R). The refraction of oxygen in the simple ether, according to Fogel' (2), is 1.764,

$$k(\mathrm{O_{ef}} - \mathrm{H})(\mathrm{C} - \mathrm{H}) = 31.7,$$

$$[M] = \frac{k(\mathrm{C} - \mathrm{H})(\mathrm{Hg} - \mathrm{H}) \cdot k(\mathrm{C} - \mathrm{H})(\mathrm{O_{ef}} - \mathrm{H})}{k(\mathrm{C} - \mathrm{H})^2} = -\frac{246 \cdot 31.7}{60} = 130^\circ.$$

This agrees well with the experimentally determined rotation of isomer I, obtained by direct addition of mercury lactate to cyclohexene.

Here we touch upon an interesting general problem—the relationship between the absolute configuration of induced asymmetric centers and the absolute configuration of the optical center in the inducer molecule, which for certain cases was studied by Prelog and Cram. In the present example, under the action of mercury S-lactate an excess of the R isomer is formed. It can be shown that the same result is obtained from direct consideration of the transition state.

The calculation of the rotation of the cis isomer is somewhat more complicated. Cis-1,2-substituted cyclohexanes represent a mixture of conformational isomers (conformers) ae and ea. The ratio of the two forms is determined by the conformational equilibrium constant, which reflects the difference in the free energies of the two conformations (18):

$$\Delta F = -RT \ln K.$$

Until now, no substituent has been known for which the axial conformation would be more favorable (19). For the benzoxymercury group, Jensen and Gale (20) found no appreciable difference between the energy of the axial and equatorial positions; nothing is known about the chloromercury group.

Fig. 2

Let us first assume that $\Delta F_{\mathrm{HgCl}} = 0$; the free-energy difference for methoxyl has been determined with a high degree of accuracy (19): $\Delta F_{\mathrm{OCH_3}} = -0.74$. From consideration of the Newman projections of the cis isomer (Fig. 2), it is seen that the two conformers make contributions to the molecular rotation equal in magnitude but of opposite sign. From the value of ΔF we find that at

equilibrium there is 77% of the conformer e-OCH_3, a-HgCl and 23% a-OCH_3, e-HgCl, whence

$$[M] = +0.77 \cdot 130^\circ - 0.23 \cdot 130^\circ = 70^\circ.$$

The rotation of diastereomer II is positive; this agrees with the fact that inversion of configuration has occurred at the asymmetric center attached to the mercury atom (racemization of RHgX by free radicals has recently been described (21)). The calculated rotation differs substantially from the experimen-

such, which apparently indicates that the assumption $\Delta F_{\mathrm{HgCl}} = 0$ is unsatisfactory. Conversely, from the data on the rotation of II one can calculate the energy difference for the equatorial and axial conformations of the HgCl group. $x \cdot 130^\circ - (1-x) \cdot 130^\circ = 45^\circ$, where x is the fraction of molecules in the conformation e-OCH_3, a-HgCl. Hence we obtain $K = 2$, and the total difference in free energies is -0.42 kcal/mole, while $\Delta F_{\mathrm{HgCl}} = -0.74 + 0.42 = -0.32$ kcal/mole. Determination of ΔF of such an order usually gives low accuracy.

On the basis of the foregoing we believe that diastereomer I is the trans form, and diastereomer II the cis form. Consequently, the reaction between cyclohexene and mercury salts proceeds by the mechanism of trans addition*.

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* Recently a report appeared (22) assigning the trans configuration to the cyclohexene adduct and the cis configuration to the norbornene adduct on the basis of NMR spectra.

Note: Figure translations are in progress. See original paper for figures.