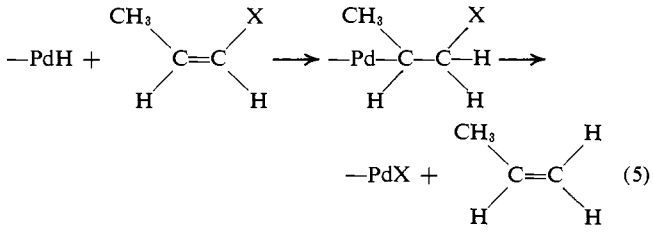
$$(C_3H_5)_2Hg + -PdCl \longrightarrow C_2H_5HgCl + -PdC_2H_5 \longrightarrow -PdH + C_2H_4 \quad (4)$$

the enol propionate tested. It was found that no isomerization occurred but rather the enol propionate disappeared. Propylene was detected as one of the products in the gas phase of the reaction vessel. This product was most likely formed by palladium(II) hydride addition followed by elimination of Pd(II) and acetate, chloride, or bromide (X = OAC, Cl, or Br).



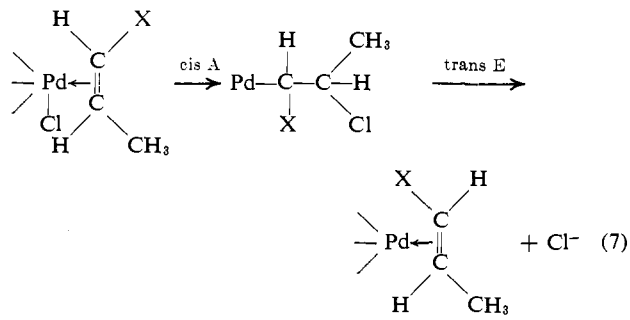
(5)

It thus appears that the mechanisms usually considered for Pd(II)-catalyzed double bond isomerizations are not operative in the present examples. It is noteworthy that the rate expression for enol propionate isomerization is consistent with a Pd(II) dimer π complex being the species which performs the isomerization. The exact mechanism whereby the π complex

$$Li_2Pd_2Cl_6 + \text{enol ester} \rightleftharpoons Li_2Pd_2Cl_5(\text{enol ester}) + LiCl \quad (6)$$

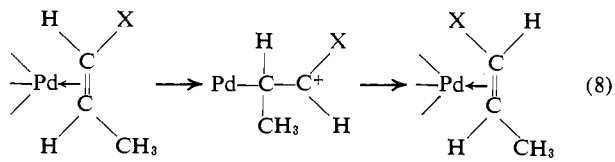
causes the isomerization is uncertain.

Possibilities include nonspecific chloropalladation (A = addition, E = elimination)



(7)

or arrangement of the π complex to a carbonium ion with sufficient lifetime for rotation. Studies aimed at elucidating the exact mechanism are presently under-



(8)

way. Whatever the mechanism, this type of isomerization will have to be considered as a possible route in the cis–trans isomerization of other olefins.

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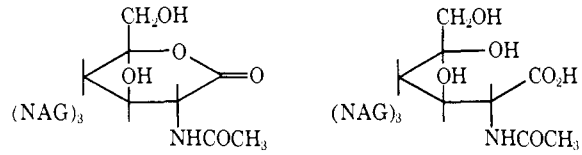
The Role of Strain in Catalysis by Lysozyme[1]

Sir:

We have prepared the lactone I derived from tetra-*N*-acetylchitotetraose[2] and have determined the association constant for its binding to lysozyme. We explain



I II

NAG = *N*-acetylglucosamine

why the magnitude of this association constant is evidence for the importance of strain in catalysis by lysozyme.

I was prepared in the following way. A solution of tetra-*N*-acetylchitotetraose[3,4] (0.005 *M*) was oxidized to the acid anion of II with iodine (0.01 *M*) in KI (0.05 *M*)–K_2CO_3 (0.045 *M*) at 4° in the dark.[5] After 3.5 hr, when titration of an acidified aliquot with sodium thiosulfate showed that 1 mol of iodine per mole of sugar had been reduced, the reaction mixture was adjusted to pH 2 with H_2SO_4, and the excess iodine was extracted with benzene. The extracted aqueous solution was adjusted to pH 7 with KOH, concentrated, and chromatographed on a Bio-Gel P-2 column, which separated the potassium salt of II (KII) from the other ions. Titration of KII gave a pK_a of 3.6 for II. Passage of KII through a cation exchange resin (Bio-Rad AG50WX-8, H^+ form) and evaporation of the eluent to dryness yielded a mixture of solid I and II. Colorimetric tests for reducing sugar[6] and amine[7] showed that the mixture contained less than 2% unreacted tetraose or deacetylated product. The lactone content and equivalent weight of the mixture were determined by rapid titration to pH 5.5, at which pH the half-time for hydrolysis of I is greater than 30 min, followed by titration to pH 9, at which pH the half-time for hydrolysis of I is less than 1 min: 23 mol % I and equivalent weight, 832 (theoretical value, 843). The concentration of I was routinely measured with the neutral hydroxylamine–ferric chloride test.[8,9]

The interaction of I with lysozyme was studied by its alteration of the protein fluorescence[10] and its inhibition of lytic activity[11] (Figure 1). The lactone was identified as by far the more potent compound in the mixture of I and II by comparing the concentration dependences of the changes in fluorescence and lytic activity before and after hydrolysis of I (see Figure 1).

(1) Supported by National Science Foundation Grant No. GB 12848.
(2) *O*-2-Acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-*O*-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-*O*-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-D-gluconic acid δ lactone.
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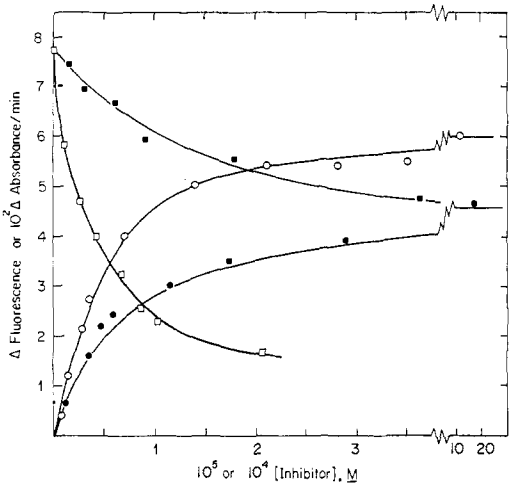

Figure 1. The interaction of the lactone I with hen egg white lysozyme. The change in the fluoresence of lysozyme (6.5×10^{-7} *M*) at 320 nm (excitation at 280 nm) in 0.005 *M* Na citrate–0.18 *M* NaCl, pH 5.0, at 23°, is plotted against the concentration of a I–II mixture with 13 mol % I (○, 10^5, *M*) or I–II mixture after hydrolysis of I at pH 9 for 30 min (●, 10^4, *M*). The rate of lysis of *M. lysodeikticus* cells (53 μg/ml) by 1.1×10^{-7} *M* lysozyme, followed by the change in absorbance at 450 nm, in 0.07 *M* Na phosphate, pH 6.2, at 30° is plotted against the concentration of a I–II mixture with 18 mol % I (□, 10^5, *M*) or a I–II mixture after hydrolysis of I at pH 6.0 in 0.3 *M* phosphate buffer for 4 hr (■, 10^4, *M*).

The dependence of the fluorescence changes upon the concentration of I obeys the equation for the formation of a 1:1 complex and yields an association constant of 3.6×10^6 M^{-1}.[10] Control experiments using the colorimetric tests for lactone[8] and reducing sugar[6] showed that during the period of measurement (about 1 min) for both fluorescence and lysis, there was less than 10% hydrolysis of the lactone and 2% cleavage of a glycosidic linkage.

On the basis of model building, Blake, *et al.*,[12] proposed that in a reactive lysozyme–substrate complex the pyranose ring which is bound in subsite D is strained from its normal chair conformation toward a half-chair conformation in which carbon atoms 1, 2, and 5, and the ring oxygen atom lie in the same plane, and that such strain is a cause of catalysis because it is relieved upon going to the transition state, which resembles an oxonium ion, the most favorable conformation for which is the half-chair one. A number of studies have supported this hypothesis.[13–17] The present study tests the strain hypothesis for the following reason: the most stable conformation for δ-lactones is the half-chair one,[18] and consequently I should bind more strongly to lysozyme in subsites A–D than the corresponding tetrasaccharide because the lactone ring can bind in subsite D without strain. In fact, the association constant for I is 36 times larger than that (10^5 M^{-1}) for tetra-*N*-acetylchitotetraose under the same conditions.[19] Moreover, the tetrasaccharide appears to bind predominantly only in subsites A–C; it thus avoids the unfavorable subsite D.[20] Studies on the binding of oligosaccharides consisting of alternating units of *N*-acetylglucosamine and *N*-acetylmuramic acid have shown that interaction of an *N*-acetylmuramic acid residue with subsite D contributes a factor of 10^{-2} to the association constant.[13] Since the factor is probably about the same for *N*-acetylglucosamine,[21] we estimate that I binds to lysozyme *3600 times more strongly* than tetra-*N*-acetylchitotetraose which is bound in the same mode (subsites A–D). Thus, relief of strain may account for a factor of 10^3–10^4 in catalysis.

Acknowledgment. We are most grateful to Dr. S. S. Lehrer for his aid in the fluorescence measurements.

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(21) The 3-lactyl side chain in subsite D probably does not interact strongly with the enzyme (ref 12).

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Structure of Chloroaquobis(trimethylarsine)tetrakis-(trifluoromethyl)rhodiacyclopentadiene. A Complex Containing Both Metal–Carbon σ Bonds and Coordinated Water

Sir:

We wish to report what we believe to be the first complete structural characterization of a solid complex containing both transition metal–carbon σ bonds and a coordinated water molecule. Previously the existence in solution of $[C_6H_5CH_2Cr(H_2O)_5]^{2+}$ [1] and $[(CH_3)_3Pt(H_2O)_3]^+$ [2] has been postulated, but no solids were isolated. More recently the complexes $[Rh(NH_3)_4(H_2O)R]SO_4$ (R = C_2H_5, C_2F_4H) have been isolated as solids and have been characterized by their infrared and nmr spectra.[3] The title compound, $RhCl(H_2O)(As(CH_3)_3)_2C_4(CF_3)_4$, is readily prepared by the decarbonylation of $RhCl(CO)(As(CH_3)_3)_2C_4(CF_3)_4$[4] in boiling benzene in the presence of moisture. It can also be prepared by exposing the yellow *solid* obtained by decarbonylating the carbonyl complex *in vacuo* at 80° (presumably $RhCl(As(CH_3)_3)_2C_4(CF_3)_4$) to moist air. The infrared spectrum of the complex shows bands due to coordinated water at 3550, 3350, and 1580 cm^{-1}, and the analytical data are in accord with the proposed formulation.[5]

The complex crystallizes from diethyl ether–petroleum ether (bp 30–60°) as pale yellow, wedge-shaped col-

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(5) *Anal.* Calcd for $C_{14}H_{20}F_{12}As_2OClRh$: C, 23.33; H, 2.80; F, 31.64; Cl, 4.92. Found: C, 23.42; H, 2.46; F, 30.33; Cl, 4.30.