species CuA^+ and B^-. It can be formed by a combination of $Cu(l\text{-}Asp)^+$ and $d\text{-}Asp^-$ or from $Cu(d\text{-}Asp)^+$ and $l\text{-}Asp^-$. Statistical arguments give

$$K_3 = \frac{[Cu(l\text{-}Asp)(d\text{-}Asp)]}{[Cu(l\text{-}Asp)^+][d\text{-}Asp^-]} = \frac{1}{2}\frac{[Cu(l\text{-}Asp)(d\text{-}Asp)]}{[CuA^+][B^-]} \quad (5)$$

(1), (4) and (5) give

$$K_2 = \frac{1}{2}K_1 + \frac{1}{2}K_3 \text{ or } K_3 = 2\left(K_2 - \frac{1}{2}K_1\right) \quad (6)$$

We have found K_1 and K_2 to be 2.82×10^6 and 1.74×10^6, respectively. Equation (6) thus gives a value of 7×10^5 for K_3, which is the formation constant of the mixed complex. The non-mixed complex is thus favored as compared to the mixed one.

Equation (6) further indicates that if the mixed complex did not form at all the value of K_2 would be one-half of K_1. Also, if no preferential formation of non-mixed complexes existed K_2 would equal K_1. And, finally, in the case that the mixed complexes were favored K_2 would be greater than K_1.

The experimental details of this and the results of further experiments will be reported in a later publication.

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A STEREOSPECIFIC CIS HYDRATION OF THE DOUBLE BOND IN CYCLIC DERIVATIVES

Sir:

The hydroboration of olefins, followed by oxidation of the product with hydrogen peroxide, provides a highly convenient procedure for the anti-Markownikoff hydration of double bonds.[1,2] In applying this reaction to cyclic olefins we have observed that the reaction proceeds stereospecifically to add the elements of water, hydrogen and hydroxyl, in a *cis* configuration to the double bond.

In this way 1-methylcyclopentene has been converted in a yield of 85% to *trans*-2-methylcyclopentanol, b.p. 152–153° at 745 mm., $n^{20}D$ 1.4488, m.p. of 3,5-dinitrobenzoate, 86–87°.[3] Similarly, 1-methylcyclohexene has been converted in a yield of 90% to *trans*-2-methylcyclohexanol, b.p. 166.5° at 745 mm., $n^{20}D$ 1.4614, m.p. of 3,5-dinitrobenzoate, 113–115°.[4,5]

In these cases the *cis* hydration results in the formation of the thermodynamically more stable isomer Consequently, the hydroboration of 1,2-dimethylcyclopentene and 1,2-dimethylcyclohexene was examined. In these cases, *cis* hydration would form the less stable isomers. 1,2-Dimethylcyclopentene yielded *cis*-1,2-dimethylcyclopentanol, b.p. 66–68° at 21 mm., m.p. 23–24°.[6] Similarly, 1,2-dimethylcyclohexene was converted into 1,2-dimethylcyclohexanol, b.p. 94° at 40 mm., $n^{20}D$ 1.4639, m.p. 24–25°.[7]

In each case the reaction products were examined by gas chromatography (glycerol column for 2-methylcyclohexanol, Carbowax column for others). In each of the four cases, the crude reaction product was shown to contain at least 97–98% of the isomer indicated, with a maximum of 2–3% of the other isomer present.

Not only does this hydration occur *cis*, but it takes place predominantly from the less hindered side of a double bond. Thus, norbornene is converted to *exo*-norborneol, m.p. 125–126°, 3,5-dinitrobenzoate, m.p. 104–105°.[8]

α-Pinene yields an alcohol, m.p. 35–38°. On basis of proposed rules, this should be isopinocamphenol.[9] Examination is continuing.

The following procedure is typical. Excess diborane (from 3.8 g. of sodium borohydride in diglyme and boron trifluoride etherate[10] was passed into 16.4 g., 0.2 mole, of 1-methylcyclopentene, b.p. 74–75° at 744 mm., $n^{20}D$ 1.4313, in 60 ml. of tetrahydrofuran at 0° over a period of two hours. After 1 hour at room temperature, several small pieces of ice were added to hydrolyze the excess diborane. The reaction mixture was immersed in an ice-bath, 45 ml. of 3 *M* sodium hydroxide was added, and then 25 ml. of 30% hydrogen peroxide, over a period of 1 hour. After 1 hour at room temperature, the upper layer was separated, the aqueous phase was extracted with ether, and the combined extracts were dried. Gas chromatographic examination of the organic phase showed the presence of 98% *trans*-1-methylcyclopentanol, with a small neighboring peak of 2% which may be the *cis* derivative. The product was isolated by fractionation in an efficient column.

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[1] H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **78**, 5694 (1956).

[2] H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1135 (1957).

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[8] K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1939), report *exo*-norborneol m.p. 128–129°, 3,5-dinitrobenzoate, m.p. 105°; *endo*-, m.p. 149–150°, 3,5-dinitrobenzoate, m.p. 123°.

[9] H. Schmidt, *Ber.*, **77**, 544 (1944).

[10] H. C. Brown and P. A. Tierney, THIS JOURNAL, **80**, 1552 (1958).

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THE SYNTHESIS OF DIPHENYLCYCLOPROPENONE

Sir:

To date no stable compound is known containing a carbonyl group in a three-membered ring. For this reason cyclopropenones are of special interest, for although the greater expected strain in the unsaturated cyclic ketones would seem likely to make them even less stable than the saturated compounds, cyclopropenones should be aromatic (being the analogs in the two-π-electron system of tropone in the six).[1] So, the preparation of a cyclo-

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[1] Our calculations, using the L.C.A.O. method with all the usual approximations, except that α_0 is taken as $\alpha_C + \beta$, show that cyclopropenone should have a vertical resonance energy of 1.4β, and that this value is essentially the same for diphenylcyclopropenone if one corrects for the stilbene system. It is thus possible that our observed stability will also be found for the simpler cyclopropenone.