TABLE II

RETENTION TIMES OF ORGANIC MATERIALS (IN MINUTES ±1 MINUTE)

Compound	152°	160°
Methylnopinol I	24	19
Methylnopinol II	28	22
Bornyl acetate	23	20
α-Fenchyl acetate	18	15
Terpinyl acetate	. .	30
Borneol	40	30
α-Fenchol	. .	20

Infrared analyses were obtained using a Perkin–Elmer model 21 recording spectrophotometer employing sodium chloride optics.

Methylnopinols.—Each isomer was recrystallized from absolute ether and its purity was established by partitioning a sample dissolved in cyclohexane.

Acetylation of Methylnopinol I.—Two grams of the alcohol dissolved in 5 cc. of acetic anhydride was heated at the steam-bath for 10 hours. The reaction mixture was decomposed with cold, saturated sodium bicarbonate solution and extracted with ether. A sample of the crude oil was partitioned by l-v.p.c. to determine the product distribution. The product was distilled to remove most of the hydrocarbons and some of the terpinyl acetate identified by its infrared spectrum. The acetate fraction of the center distillation cut was then removed by repetitive partitioning of 50-μl. portions. The material collected was twice repartitioned, yielding a colorless oil of n^{22}D 1.4550 shown to be α-fenchyl acetate by comparison of its infrared spectrum with that of an authentic sample. The acetate (0.100 g.) was allowed to stand overnight in methanolic potassium hydroxide. The methyl alcohol was boiled off, and the residue was taken up in ether. The oil remaining after evaporation of the ether was partitioned, yielding a partially solid material shown to be α-fenchol by its infrared spectrum.

Acetylation of Methylnopinol II.—Three grams of methylnopinol dissolved in 5 cc. of acetic anhydride was heated for five hours at the steam-bath. The product was treated as described above for isomer I. Multiple partitioning of the minor acetate fraction provided a partially solid material indicated to be bornyl acetate by its infrared spectrum. To 0.10 g. of acetate dissolved in 2–3 cc. of absolute ether was added a small lump of lithium aluminum hydride. After several hours water was added to decompose the excess hydride, and the ether layer was removed and evaporated. The residue was dissolved in cyclohexane and partitioned, yielding a single crystalline solid melting at 200–203° and shown to be borneol by its infrared spectrum.

Acetylation of the Magnesium Salt of Methylnopinol II.—A solution of 1.0 g. of the methylnopinol in 10 cc. of ether was added dropwise to a solution of *n*-propylmagnesium bromide prepared by adding 1.6 g. of *n*-propyl bromide in 10 cc. of ether to 0.35 g. of magnesum ribbon. After all of the alcohol had been added the mixture was refluxed gently for one hour. Acetic anhydride (2.0 g. in 10 cc. of ether) was added slowly with cooling and the reaction mixture was allowed to stand for two days at room temperature. The product was removed by steam distillation of the reaction mixture and treated as described for the other acetate preparations. The partitioned acetate was shown to be bornyl acetate by its infrared spectrum and by its conversion to borneol by lithium aluminum hydride.

Acknowledgment.—The methylnopinol samples were provided by Professor Saul Winstein, to whom we are deeply grateful.

STANFORD, CALIF.

COMMUNICATIONS TO THE EDITOR

FORMATION CONSTANTS OF METAL COMPLEXES CONTAINING OPTICALLY ACTIVE LIGANDS[1]

Sir:

It has been observed by other workers[2] that metals (M) when combining with optically active ligands (*l*-X) and (*d*-X) form complexes of the type $M(l\text{-X})_n$ and $M(d\text{-X})_n$ rather than the mixed complex $M(l\text{-X})_n(d\text{-X})_m$.

To demonstrate whether this favoring of non-mixed complexes occurs, at equilibrium, in solution the author has measured the formation constants of both types of complex. Two potentiometric titrations were made[3]: (1) the titration of a 2:1 mixture of *l*-asparagine and copper (II) with potassium hydroxide and (2) the titration of a 2:1 mixture of racemic-asparagine and copper(II) ion. In the first case the constant

$$K_1 = \frac{[\mathrm{Cu}(l\text{-Asp})_2]}{[\mathrm{Cu}(l\text{-Asp})^+][l\text{-Asp}^-]} \qquad (1)$$

$\mathrm{Asp}^- =$ negative ion of asparagine

could be calculated by conventional methods. In the second case the same calculations would give the constant

$$K_2 = \frac{[\mathrm{Cu}(l\text{-Asp})_2] + [\mathrm{Cu}(d\text{-Asp})_2] + [\mathrm{Cu}(l\text{-Asp})(d\text{-Asp})]}{\{[\mathrm{Cu}(l\text{-Asp})^+] + [\mathrm{Cu}(d\text{-Asp})^+]\}\{[l\text{-Asp}^-] + [d\text{-Asp}^-]\}} \qquad (2)$$

It is to be expected that

$$[\mathrm{Cu}(l\text{-Asp})_2] = [\mathrm{Cu}(d\text{-Asp})_2]$$

and

$$[\mathrm{Cu}(l\text{-Asp})^+] = [\mathrm{Cu}(d\text{-Asp})^+] \qquad (3)$$

and

$$[l\text{-Asp}^-] = [d\text{-Asp}^-]$$

thus

$$K_2 = \frac{[\mathrm{Cu}(l\text{-Asp})_2]}{2[\mathrm{Cu}(l\text{-Asp})^+][l\text{-Asp}^-]} + \frac{1}{4}\,\frac{[\mathrm{Cu}(l\text{-Asp})(d\text{-Asp})]}{[\mathrm{CuA}^+][\mathrm{B}^-]} \qquad (4)$$

where $\mathrm{A}^- = l\text{-Asp}^-$ if $\mathrm{B}^- = d\text{-Asp}^-$

and $\mathrm{A}^- = d\text{-Asp}^-$ if $\mathrm{B} = l\text{-Asp}^-$

The second term of (4) represents the formation constant of the mixed complex from the mixed

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[1] This investigation was supported in part by a research grant RG 5532 from the Division of General Medical Sciences, Public Health Service.

[2] Fred Basolo, "The Chemistry of the Coördination Compounds," Edited by John C. Bailar, Jr., Reinhold Publishing Corp., New York, N. Y., 1956, p. 313.

[3] The conditions were at a constant ionic strength of 0.1 (maintained by KCl) and at 25°.

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

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

(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., $n^{20}\text{D}$ 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., $n^{20}\text{D}$ 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., $n^{20}\text{D}$ 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., $n^{20}\text{D}$ 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).

(3) W. Hückel and H. D. Sauerland, *Ber.*, **87**, 1003 (1954), report b.p. 149–151.2° at 735 mm., $n^{20}\text{D}$ 1.4501, m.p. of 3,5-dinitrobenzoate, 88°.

(4) M. G. Vavon, A. Perlin and M. A. Horeau, *Bull. Soc. chim. France*, **51**, 644 (1932), report b.p. 165° at 750 mm.

(5) L. M. Jackman, A. K. Macbeth and J. A. Mills, *J. Chem. Soc.*, 1717 (1949), report $n^{20}\text{D}$ 1.4616, m.p. of 3,5-dinitrobenzoate, 117°.

(6) L. W. Trevoy and W. G. Brown, THIS JOURNAL, **71**, 1675 (1949), report *cis*-1,2-dimethylcyclopentanol, b.p. 62° at 17 mm., m.p. 24–26°; *trans*-, b.p. 51° at 17 mm., m.p. 24–25°.

(7) G. Chiurdoglu, *Bull. Soc. chim. Belg.*, **47**, 241 (1938), reports *cis*-1,2-dimethylcyclohexanol, b.p. 82.8° at 25 mm., $n^{20}\text{He}$ 1.4649, m.p. 23.2°; *trans*-, b.p. 74° at 25 mm., $n^{20}\text{He}$ 1.4614, m.p. 13.2°.

(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.