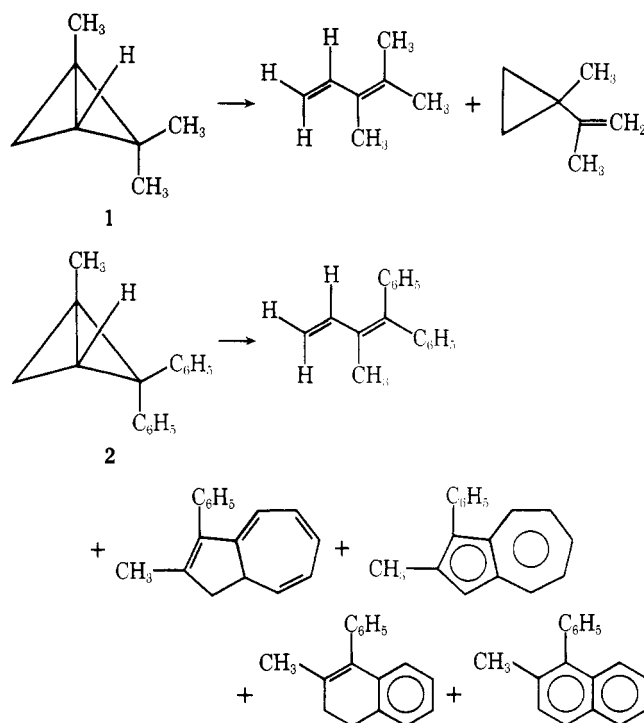# *Communications*

Kinetic Resolution via the Transition Metal Complex Promoted Rearrangement of Strained Hydrocarbons

Summary: Chiral rhodium (DIOP) chloride complexes have been shown to selectively promote the rearrangement of one enantiomer of racemic bicyclo[1.1.0]butane derivatives. This kinetic resolution has been shown to give greater than 30% enantiomeric excess. A chiral shift reagent was used to determine the amount of resolution.

Sir: The use of optically active transition metal complexes to promote reactions in which achiral or racemic starting materials are converted into optically active hydrocarbons has recently received considerable attention.[1] This is particularly true in the area of catalytic reductions with homogeneous, optically active, Wilkinson[2] type catalysts.[1,3,4] In addition, a few isolated examples exist in which optically inactive olefins or acetylenes have been isomerized over chiral catalysts to yield optically active products.[5] We now wish to report what we believe to be the first examples of transition metal complex promoted kinetic resolution of highly strained hydrocarbons.

We had previously demonstrated that certain rhodium(I) complexes promoted the rapid rearrangement of 1,2,2-trimethylbicyclo[1.1.0]butane (1)[6] and 1-methyl-2,2-diphenylbicyclo[1.1.0]butane (2)[7] into the products shown. Our desire for optically active variants of 1 and 2 prompted us to explore the possibility of a kinetic resolution based on the selective isomerization of one member of each of the enantiomeric pairs 1 and 2. In order to accomplish our objectives, we prepared the diphosphinerhodium(I) complexes from both (+)- and (-)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (hereafter referred to as DIOP) according to literature procedures.[8] It was found that Rh(DIOP)Cl promoted the rapid isomerization of both 1 and 2.

In order to determine the degree of kinetic resolution obtained when chiral DIOP complexes were used, it was necessary to develop a method for establishment of the enantiomeric excess (ee) which existed after partial rearrangement of 1 and 2. The method of analysis, which we developed, involved treatment of the residual bicyclo[1.1.0]butane, 1 or 2, with *n*-butyllithium in ether followed by addition of methyl chloroformate to yield 3 or 4, respectively.[9] Nuclear magnetic resonance spectral analysis of 3 and 4 in the presence of the chiral shift reagent, tris[3-(trifluoromethylhydroxymethy-

lene)-*d*-camphorato]europium(III) resulted in the clean separation of both of the enantiomeric *exo*-methyl resonances and of the corresponding methoxyl group resonances of 3, and of both of the enantiomeric bridgehead methyl resonances and of the corresponding methoxyl group resonances of 4. This
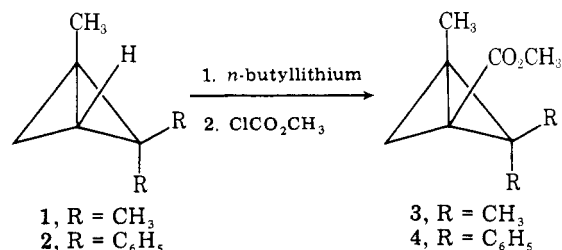
provided a double check on the enantiomeric excesses which we hoped to generate.

Table I lists the degree of kinetic resolution observed for

Table I. Kinetic Resolution of Racemic Bicyclo[1.1.0]butanes Using Rh(DIOP)Cl Complexes

Compd	DIOP	Time	Temp, ±2 °C	% conv[a]	% enantiomeric excess (±5)	$[\alpha]^{25}_D$ [b]
1	(−)[c]	9 h	0	61	2	+0.48
1	(+)[d]	9 h	0	40[e]	4[f]	−0.84
2	(−)[g]	30 d	4	56	18	−23.2
2	(+)[g]	18 d	4	53	17	+25.3
2	(−)[g]	22 h	24	62	33	−43.6
2	(+)[g]	17 h	24	73	35	+45.5

[a] % conversion was determined by NMR analysis vs. an internal standard. [b] Rotations were measured in carbon tetrachloride (c 0.5–5.0) using a Perkin-Elmer recording polarimeter model 241. [c] Reaction run in 3:4 v/v veratrole/diethyl ether. [d] Reaction run in 3:2 v/v veratrole/diethyl ether. [e] The percent conversion varied considerably from run to run due to the sensitivity of the reaction to the presence of oxygen. [f] The percent enantiomeric excess for 3 is less than the error factor in determining these values by NMR analysis. Thus, the agreement of the rotation of 3 with the determined percent enantiomeric excess may be fortuitous. [g] Chloroform as solvent.

both **1** and **2** with both (+)- and (−)-DIOP complexes. As noted in the table, the degree of kinetic resolution in the rearrangement of **1** was very small, but it did exist. In contrast, the diphenyl-substituted bicyclo[1.1.0]butane (**2**) showed excellent sensitivity to the chirality of the transition metal complex. The development of greater than 30% enantiomeric excess in this kinetic resolution indicates to us that the transition metal complex promoted rearrangement of strained hydrocarbons may be extremely sensitive to steric factors.[10,11]

In summary, we have provided the first example of a kinetic resolution of a strained polycyclic compound. Our procedure makes optically active derivatives of bicyclo[1.1.0]butane readily available for the first time. We hope that this process can be extended to the kinetic resolution of other highly strained polycyclic hydrocarbons.

References and Notes

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(9) Satisfactory spectral data, elemental analysis, and exact mass molecular weight were obtained for both **3** and **4**. Racemic **4** has mp 57–58 °C.

(10) We were somewhat surprised that the selectivity appeared to be less at 4 °C than it was at 24 °C. We can only theorize that during the extremely long time required for rearrangement at the lower temperature, some of the starting material may have been consumed in nonmetal promoted rearrangements.

(11) While the exact absolute rotation of **4** cannot be determined due to the error limits in determining the enantiomeric excess by NMR, it can be assumed that the value will be in the 130–140° range.

(12) Lando Undergraduate Scholar, Summer, 1975.

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