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KINETIC RESOLUTION OF DIALKYLCYCLOPROPANES

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The preparation of optically-active cyclopropanes has continued to attract wide attention. Recent publications have focused upon the preparation of cyclopropyl carboxylates using chiral catalysts[1] or chiral diazoacetates.[2] The synthesis of chiral dialkylcyclopropanes has required optically-active starting materials[3] or the resolution of a cyclopropyl carboxylate with subsequent conversion to the desired cyclopropane.[4] The direct resolution of dialkylcyclopropanes had not been realized. In this paper, we described the kinetic resolution of trans-1,2-dimethylcyclopropane by the enantioselective destruction of platinacyclobutanes with chiral phosphines and chiral olefins.

The platinacyclobutane $\underset{\sim}{1}$ was prepared from trans-1,2-dimethylcyclopropane and Zeise's dimer according to literature procedures.[5] Treatment of $\underset{\sim}{1}$ in THF with 0.5 equiv of a chiral phosphine or olefin resulted in the partial destruction of the platinacycle with concurrent formation of the optically-active trans-1,2-dimethylcyclopropane. The residual platinacycle could be treated with 0.5 equiv of triphenylphosphine and resulted in recovery of the enantiomeric cyclopropane. Hence, this method of resolution results in the ready separation of both enantiomers without destruction of one of the enantiomers as is often the case with kinetic resolutions. The results are summarized in Table I

As the formation of the platinacycle $\underset{\sim}{1}$ is nearly quantitative and the destruction is likewise nearly quantitative,[6] this represents an excellent method of kinetic resolution without destruction of one of the enantiomers. Furthermore, this is, to our knowledge, only the second example of the resolution of an organic substrate which is devoid of a carboxyl or similar functional group by which to effect the resolution.[7] The earlier example, however, resulted in destruction of one of the enantiomers whereas this method allows for the ready recovery of both enantiomers. We are continuing to explore this method of resolution for other cyclopropanes

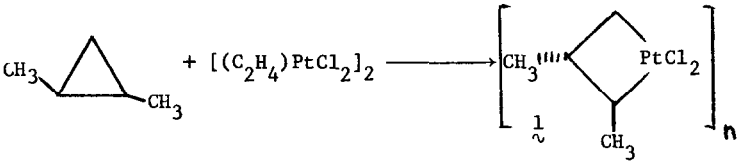

Table I. Kinetic Resolution of trans-1,2-Dimethylcyclopropane via 1 and Chiral Reagents.

Chiral Reagent	%ee[a]	Isomer[b]	%ee, Residual Isomer[c]
(+)-DIOP[d]	35	RR	31
(-)-DIOP[d]	31	SS	27
(+)-NMDPP[e]	21	RR	17
(+)-CAMPHOS[f]	10	RR	9
(-)-β-Pinene	5	SS	5
(-)-Carvone	12	SS	8
(+)-Carvone	10	RR	7
(+)-Limonene	15	RR	12

(a) % Enantiomeric excess, determined by the method of von E. Doering.[3] (b) Per the assignment of von E. Doering.[3] (c) Obtained by the treatment of residual 1 with triphenylphosphine. (d) Prepared by the method of Kagan.[8] (e) Prepared by the method of Morrison.[9] (f) Prepared by the method of Morrison.[10]

References and Notes

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(6) The production of cyclopropane is accompanied by a small amount of olefin. At room temperature, the olefin products constitute less than 5% of the products but will begin to predominate at higher temperatures.

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