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(4) We have no proof for the competitive reduction of **2** and hydrogenolysis of **4**. However, the quantitative conversion of **5** to **6** demonstrates that the enol ether functionality is quite receptive to catalytic reduction; and thus it seems that some of the alkene bond of **2** might suffer similar reduction.

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(7) The stereochemistry of the products formed from this reaction is not yet known.

Studies Directed toward a Practical Synthesis of Brevicomin. V. Isomer Enrichment of Bicyclic Ketals in the 6,8-Dioxabicyclo[3.2.1]octane Series by Complexation with Titanium Tetrachloride

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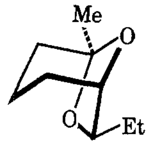
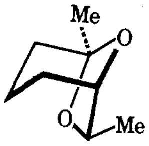
As part of a continuing effort directed toward a practical synthesis of brevicomin (1),[1] the aggregating sex pheromone of the pine bark beetle, *Dendroctonus brevicomis,* we initiated a study of methods for effecting isomer enrichment. Since it is well documented that powerful synergistic effects are noted for compound mixtures in testing, an effective method to remove unwanted isomers became quite important.[2] In our synthetic methodologies to date, we have always prepared a mixture isomeric about C-7.

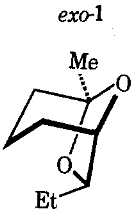
Since 1 has proven to be relatively difficult to obtain in quantity at this time, we chose to study the readily available 2 for our isomer enrichment study.[3]



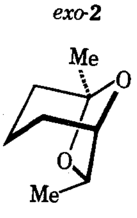
exo-**1**



exo-**2**



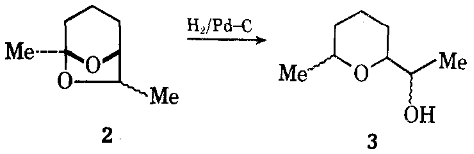
endo-**1**



endo-**2**

Substituted 1,3-dioxolane and dioxane derivatives have been generally observed to suffer cleavage and rearrangement to an appropriate ester in the presence of titanium tetrachloride.[4] Though this is a well-known Lewis acid capable of complexing ligands having heteroatom functionality,[5] *no ketal complexation has been reported.* We have observed, however, that titanium tetrachloride readily forms a complex with 2, and this complex can be hydrolyzed with water to recover 93% of the initial bicyclic ketal.

We had previously noted[6] that hydrogenolysis of *endo*-2 proceeded much faster than *exo*-2 (2 → 3). This was rationalized as a steric effect of the exo methyl group on the catalyst surface. Taking advantage of this observation we envisioned preparing a $TiCl_4$ "surface" on which one isomer might selectively interact. This was accomplished by preparing a dilute $TiCl_4$–CCl_4 frozen matrix at liquid nitrogen temperature. Typically, 0.005 mol of $TiCl_4$ in 20 ml of carbon tetrachloride was frozen in liquid nitrogen. To the surface formed was added 0.01 mol of ketal, and the solution was allowed to warm, unperturbed, to room temperature. The complex was filtered through a fritted glass filter and the filtrate was reduced in volume. GLC analysis indicated, that as expected, the endo isomer was selectively complexed. Hydrolysis of the filtered complex with water, followed by extraction with methylene chloride, yielded an enriched endo-isomer mixture. If the experiment is carried out without solvent, selectivity is decreased. This enrichment procedure can be repeated as many times as necessary to reach a desired isomeric purity. Starting with 2 having an exo–endo ratio of 15.9:9.4, three cycles increased the ratio to 16:2.7. This constitutes an enrichment of 71.5% by an experimentally simple procedure.



2 3

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Registry No.—1, 20290-99-7.

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Radical Decomposition of α-Hydroperoxy Ketones. A Facile Scission of Benzoyl Radical[1]

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The β-scission of *tert*-alkoxy radicals has been established,[2] and previous reports include the information on the scission of halomethyl,[2a,h] alkoxymethyl,[2h,i] and alkoxycarbonyl radicals,[2h,i] and of acyl radical.[3,4] In the course of our study on the basic decomposition of α-hydroperoxy ketones,[5] **1**, the facile fission of benzoyl radical was observed.