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THE TRANSITION METAL COMPLEX INDUCED REARRANGEMENT OF BICYCLO[2.1.0]PENTANE TO CYCLOPENTENE

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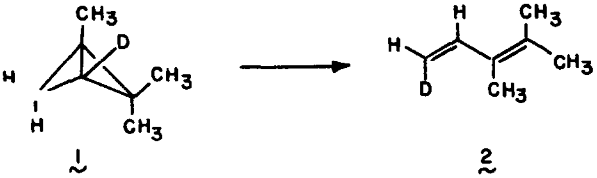
Cyclobutane to diolefin transformations promoted by transition-metal compounds, such as the isomerization of quadricyclanes to norbornadienes[1-3] and of cube type molecules to ring cleaved products,[4,5] have recently attracted considerable attention. Lately, we[6] and others[7] have explored the related isomerizations of derivatives of bicyclo[1.1.0]butane, such as that exemplified by the stereospecific conversion of 1 to 2 on addition of rhodium dicarbonyl chloride dimer or dichlorotricarbonylruthenium dimer.[6] We now wish to report the first example of the transition-metal promoted isomerization of a simple bicyclo[2.1.0]-pentane.



Bicyclo[2.1.0]pentane[8] (3) possesses surprising thermal stability. It can be prepared pyrolytically from 2,3-diazabicyclo[2.2.1]hept-2-ene (4) at 200° with no detectable thermal isomerization.[9] Criegee reported[8] that 3 was isomerized to cyclopentene (5) in the vicinity of 330°. We have now found that bicyclo[2.1.0]pentane is extremely labile in

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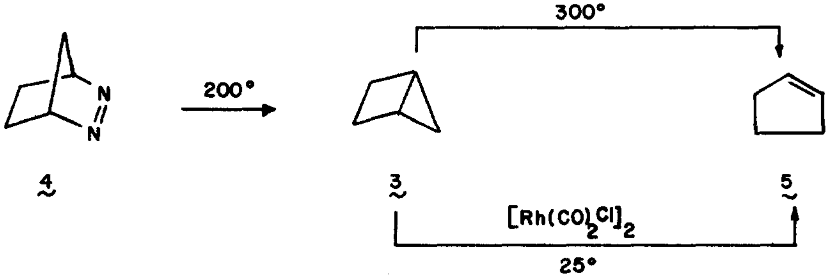
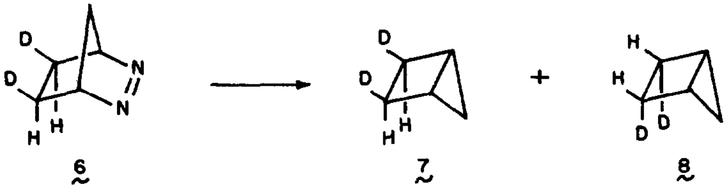
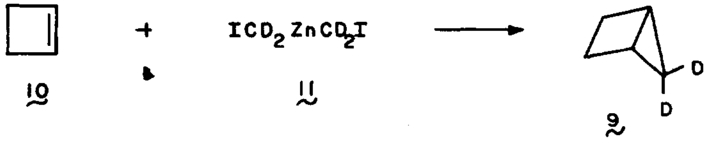


the presence of rhodium dicarbonyl chloride dimer.[10] When 3 was treated with 5 mol % of rhodium dicarbonyl chloride dimer in either acetonitrile or chloroform at 25° (room temperature), isomerization to 5 occurred with a half-life of *ca.* 8 hr. At 65°, no trace of 3 could be detected after 48 hr in the presence of 2 mol % of transition metal compound. Vpc analysis indicated that the isomerization of 3 to 5 was quantitative.

In order to study some of the mechanistic aspects of this facile rearrangement we desired certain isotopically labelled versions of 3. Synthesis of 6 according to literature procedures[11] followed by pyrolysis at 200° gave a 2.9:1 mixture of 7 and 8.[12] Irradiation of 6 in an *n*-butanol glass at *ca.* -70° gave a 1.3:1 mixture of 7 and 8.[12] Synthesis of 5,5-dideuteriobicyclo[2.1.0]pentane (9) was accomplished through the reaction of





cyclobutene (10) with 11.[13] This procedure gave material which was 84% dideuterated.

When we subjected either the 2.9:1 mixture of 7 and 8, the 1.3:1 mixture of 7 and 8, or 9 to rhodium dicarbonyl chloride dimer, we found that the same mixture of deuterated cyclopentenes was found. For instance, it was shown by nmr spectroscopy that both mixtures, and 9, gave cyclopentene in which the ratio of vinylic hydrogens to hydrogens on saturated carbon was 1:3.21 ± 0.09. A purely random distribution of the two deuteriums would have given a ratio of 1:3, assuming no deuterium isotope effect on the ratio. It was demonstrated that the observed ratio was not due to rearrangement followed by scrambling of the free deuterated cyclopentenes, through the subjection of 1-deuteriocyclopentene (12)[12] to the reaction conditions. After four half-lives, no isomerization of 12 could be detected. This indicated that the deuterium scrambling must have occurred at an intermediate stage, when the transition metal complex was associated with the C_5H_8 moiety, and before the cyclopentene was freed from the transition metal complex.

Our studies indicate that ring systems with considerably less strain energy than quadricyclanes, cubanes, and bicyclo[1.1.0]butanes are susceptible to rearrangements promoted by transition metal complexes. Furthermore, our isotope studies indicate that extensive rearrangement may rapidly follow the initial cleavage of the strained ring system.

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