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TRANSITION METAL CATALYZED ISOMERIZATION OF SUBSTITUTED BICYCLO[2.1.0] PENTANES[1]

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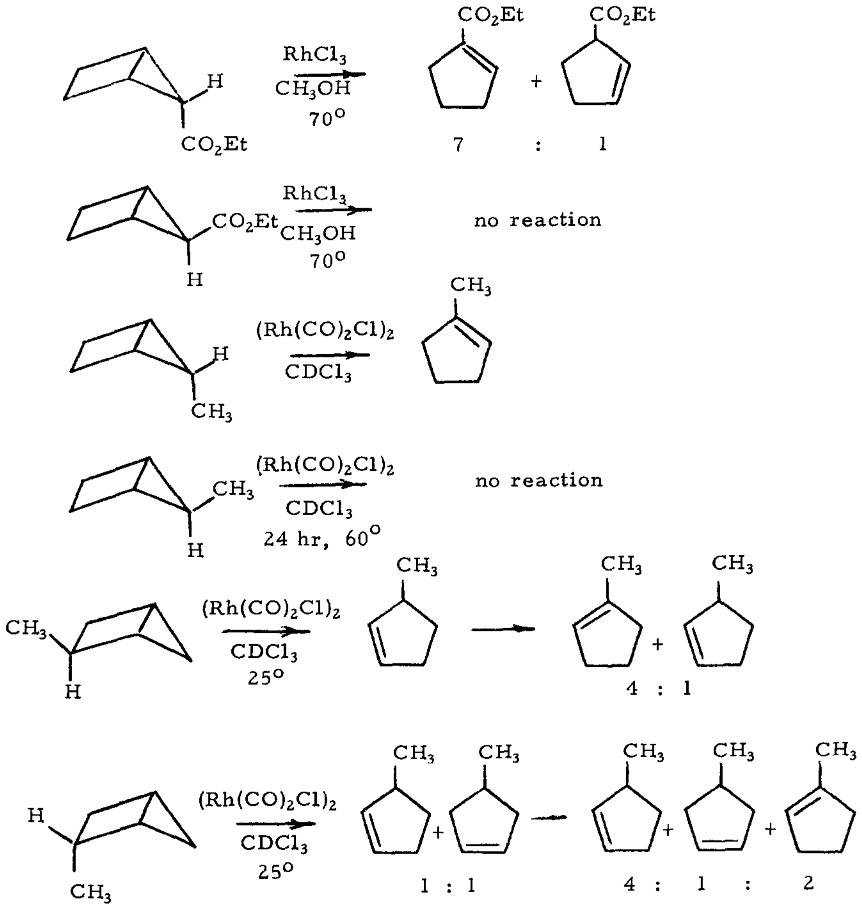
The isomerization of strained cyclic compounds by metal ions has received much study.[3,4] We should like to present evidence which points to the role of transition metal hydrides as intermediates in some of these reactions.

The transition metal catalyzed rearrangement of bicyclo[2.1.0]pentane has been shown by Gassman, Atkins and Lumb to give cyclopentene as the only product.[5] We have found that whereas $(P\phi_3)_2RhCl$, $Ir(CO)(P\phi_3)_2Cl$, $RuCl_3$, $IrCl_3$ and Na_2PtCl_6 are effective in catalyzing the rearrangement, the following typical Lewis acid catalysts were inactive under comparable conditions: Fe(III), Ni(II), Cd(II), Zn(II), Mg(II), Hg(II) and Ag(I). When $RhCl_3$[6] was used as the catalyst in methanol-d solution, the cyclopentene formed had 30% d_1, 26% d_2, 14% d_3 and 6% d_4. The high deuterium incorporation almost certainly involves a metal hydride.[7] It is known that such hydrides will exchange hydrogens with the hydroxylic protons of methanol.[8] Thus, once the hydride is formed it may be converted to the deuteride by reaction with methanol-d. Multiple deuterium incorporation probably involves further reaction of cyclopentene with the metal deuteride. Gassman, et al.[5] found cyclopentene-d_1 to undergo deuterium scrambling when present during the bicyclopentane isomerization, and have suggested that a metal hydride is involved in this process.

In order to gain further information concerning the role of transition metal hydrides in the isomerization of bicyclo[2.1.0]pentane, the reactions of a number of substituted derivatives have been examined. The 5-carbethoxybicyclo[2.1.0]pentanes were prepared as previously described,[9] and were reduced to the corresponding carbinols. Oxidation of the latter to the aldehyde with the chromium trioxide-pyridine complex,[10] followed by a Wolff-Kishner reduction[11] gave the 5-methyl derivatives.[12] The 2-methyl derivatives were prepared as previously described.[13]

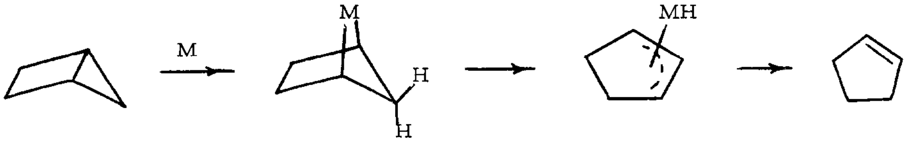
The results of rhodium catalyzed isomerization are summarized below:



$$k_{endo}/k_{exo} = 5$$

The carbethoxy derivatives did not react at room temperature, and at 70°, the endo-isomer reacted readily whereas the exo-isomer gave no appreciable reaction. The endo-5-methyl derivative was more reactive, but again, the exo-isomer was unreactive. The initial products of the isomerization were isomerized as shown above under the reaction conditions.

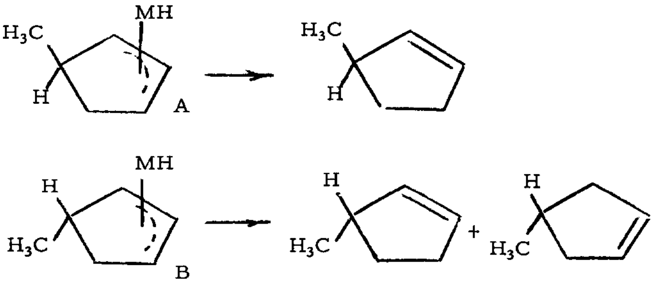
These results point to the importance of the 5-exo-hydrogen in the isomerization, and lends support to the following path for the reactions:



The first step, in analogy with other transition metal isomerizations,[4] is probably an oxidative addition across the central bond of the hydrocarbon. Abstraction of the exo-hydrogen would generate an allyl-rhodium hydride. This type of complex has been shown to decompose to an olefin and a metal complex,[14] and such a reaction would lead to the observed product, cyclopentene. The intermediate allyl-rhodium hydride would be responsible for the exchange with methanol-d, and for the isomerization of substituted cyclopentenes.

In order to test the possibility that the oxidative addition is reversible and that the hydrogen transfer step is rate determining, the isomerization of a mixture of 5-carbethoxybicyclo[2.1.0]pentane and 5-carbethoxybicyclo[2.1.0]pentane-d_5 (prepared using ethyl diazoacetate-d_1) was carried out. The progress of the reaction was followed mass spectrometrically, and the ratio of the labeled and unlabeled esters remained constant. The absence of a kinetic isotope effect indicates the oxidative addition to be rate determining with the carbethoxy derivative.

The difference in products found with the exo- and endo-2-methylbicyclo[2.1.0]-pentanes is of particular interest, and fit well with the proposed mechanism. In species A, formed from the exo-isomer, steric repulsion between the metal and the methyl group will favor transfer of the metal-bound hydride to the least hindered end of the allyl system. On the other hand, with the intermediate B formed from the endo-isomer hydrogen transfer is equally likely in both directions, leading to the observed 1 : 1 mixture of alkenes.



References

1. This investigation was supported by a grant from the National Science Foundation.
2. N. I. H. predoctoral fellow, 1969-1972.
3. L. A. Paquette, *Accts. Chem. Res.*, **4**, 280 (1971).
4. J. Halpern, *Accts. Chem. Res.*, **3**, 386 (1970).
5. P. G. Gassman, T. J. Atkins and J. T. Lumb, *Tetrahedron Lett.*, 1643 (1971); *J. Amer. Chem. Soc.*, **94**, 7757 (1972).
6. Rh(I) is presumably the catalyst since it has been shown that Rh(III) is quickly reduced to Rh(I) during olefin isomerization in ethanol. H. Hirai, H. Sawai, E. I. Ochiai and S. Makishima, *J. Catalysis*, **17**, 119 (1970).
7. J. F. Harrod and A. J. Chalk, *J. Amer. Chem. Soc.*, **86**, 1776 (1964).
8. R. Cramer and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **88**, 3534 (1966).
9. K. B. Wiberg and A. J. Ashe, III, *J. Amer. Chem. Soc.*, **90**, 63 (1968).
10. R. Radcliff and R. Rodehurst, *J. Org. Chem.*, **35**, 4000 (1970).
11. R. T. LaLonde and A. D. Debboli, Jr., *J. Org. Chem.*, **35**, 2657 (1970).
12. D. H. White, P. B. Condit and R. G. Bergman, *J. Amer. Chem. Soc.*, **94**, 7931 (1972) prepared the 5-methyl derivatives by a different route. We thank Prof. Bergman for providing spectra of these compounds.
13. J. P. Chesick, *J. Amer. Chem. Soc.*, **84**, 3250 (1962). The *exo* and *endo*-geometries were tentatively assigned based on the nmr spectra. Our examination of the spatial relationship between the methyl group and the cyclopropane ring suggests that the nmr chemical shifts may be an unreliable guide to geometry in this case. We prefer to assign the *endo*-structure to the isomer which is less stable at equilibrium.
14. J. F. Nixon and B. Wilkins, *J. Organometal. Chem.*, **44**, C25 (1972).