RHODIUM (I) CATALYZED VALENCE ISOMERIZATION OF QUADRICYCLANES

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It has been known for some years that transition metal complexes of Rh^I and Pd^{II} catalyse the formally "orbital symmetry forbidden" isomerization of quadricyclane (I) to norbornadiene (II).[1] In contrast, the $Rh_2(CO)_4Cl_2$ catalyzed isomerization of the 3-oxaquadricyclane III leads to the hydroxyfulvene IV.[2]


$$E = CO_2CH_3$$
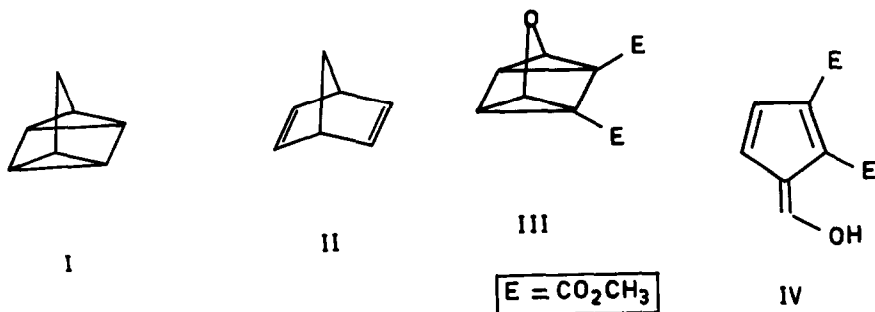
To obtain a better insight into the reasons for the difference of the above mentioned two reactions, we started a study of the rhodium (I) catalyzed reactions of a series of substituted quadricylanes I, V, VI and VII,   prepared according to literature procedures.[3,4,5]
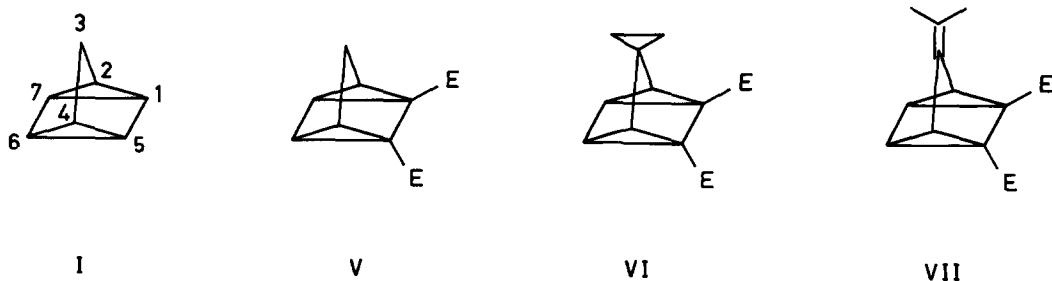
We wish now to report the results. The series was selected so as to bridge gradually the difference between compounds I and III, that is, the presence of two ester groups and an 0-atom instead of a C-atom at position 3 of the quadricyclane. Compound V differs from I only in the former aspect, and in going from V $\longrightarrow$ VI $\longrightarrow$ VII the C-3 atom increases in electronegativity[6] so as to approach the 0-atom.[7] Treatment of I, V, VI and VII with cataly-tic amounts (5 mol%) of $Rh_2(norbornadiene)_2Cl_2$ or $Rh_2(CO)_4Cl_2$ in $CDCl_3$ leads in all cases quantitatively to the corresponding norbornadienes II, VIII, IX and X.
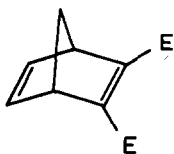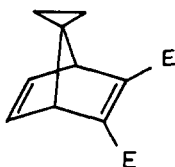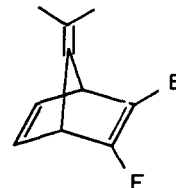

| II | VIII | IX | X |

Although there is no difference in the kind of product being formed, the temperature at which the isomerization occurs differs strongly for I and for V, VI and VII. We have determined the second order rate constants[9] of the isomerization of the quadricyclanes in $CDCl_3$, by following the conversion with N.M.R. spectroscopy, using $Rh_2(norbornadiene)_2Cl_2$ as the catalyst. The re-sults are reported in the Table.

Table. Second order rate constants[11] of the isomerization of the quadricyclanes I, V, VI and VII into the corresponding norbornadienes II, VIII, IX and X. Catalyst concentration: 0,03 M.

compound	$10^2k_2(M^{-1}.s^{-1})$	temperature (°C)	relative rate
I	5,5	-26	5000
V	0,6	45	
	1,4	60	1
VI	0,4	38	
	0,7	45	
	1,0	52	
	1,7	60	1,2
	$1,3 \times 10^{-3}$ a)	-26	
VII	0,6	60	0,4

a) extrapolated value by use of the Arrhenius relation ($E_a = 14$ kcal/mole, $A = 2 \times 10^7$ $M^{-1}.s^{-1}$)

From the table one observes, that substituents at position 3 have little influence on the rate

of isomerization. This is not surprising since position 3 is not adjacent to the reaction centers,

these being carbon atoms 1 and 7 (or 5 and 6) in the oxidative addition mechanisms.[10] However, the

introduction of the two ester substituents causes a dramatic lowering of the rate, which will be

the result of steric and electronic effects, as found previously in some other cases.[12] It is

important to note that the two ester substituents have a much greater rate retarding effect in

the quadricyclane than in the cubane series[12a] (5000 and 120, respectively). This is probably

due to the fact, that in the former case one of the ester substituents is bonded to a C-atom

that is complexed to the rhodium atom, whereas this need not be the case in the cubane series.
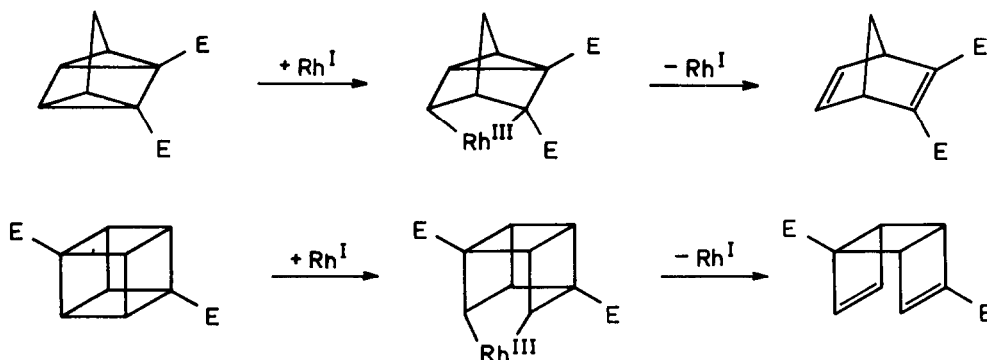

The different product formation on treating I, V, VI and VII with Rh[I]-catalyst on one hand and

treating III with Rh[I]-catalyst on the other hand, may be explained in terms of kinetic versus

thermodynamic control. The norbornadienes are thermodynamically less stable than the isomeric

fulvenes[13,14]: compound III gives -as the sole product- the thermodynamically more stable fulvene

IV, whereas the compounds I, V, VI and VII give the thermodynamically less stable norbornadienes

II, VIII, IX and X, respectively. It is therefore reasonable to surmise, that the former iso-

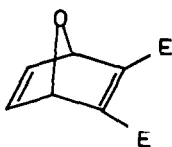merization is thermodynamically controlled, but that the latter is kinetically controlled.

References and notes.

1. H. Hogeveen and H.C. Volger, J.Am.Chem.Soc. 89, 2486 (1967).

2. A. Bruggink and H. Hogeveen, Tetrahedron Lett. 1972, 4961.

3. G. Kaupp and H. Prinzbach, Helv.Chim.Acta 52, 956 (1969).

4. O. Diels and K. Alder, Ann. 490, 236 (1931).

5. G. Kaupp and H. Prinzbach, ibid. 725, 52 (1969).

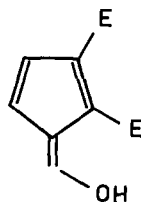6. M.G. Brown, J.Chem.Phys. 33, 1881 (1960) and literature cited.

7. It has been reported[8] that compound VII reacts under the influence of $AgBF_4$ in CH_2Cl_2, to form both the corresponding norbornadiene X, as well as the cyclopentadienyl-allene XI, so that under these conditions the reactivity pattern lies in between those of V and III.
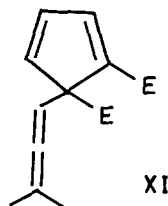
8. S.F. Nelson, J.P. Gillespie and P.J. Hintz, Tetrahedron Lett. 1971, 2361.

9. According to Cassar and Halpern[10], the Rh_2(norbornadiene)$_2Cl_2$ catalyzed isomerization of I follows the second order catalytic rate law: $\frac{-dI}{dt} = k_2[I]$ [catalyst].

10. L. Cassar and J. Halpern, Chem.Comm. 1970, 1082.

11. They represent composite rate constants, being the product of a pre-equilibrium constant and a rate determining step constant. H. Hogeveen and B.J. Nusse, to be published.

12. a) for Rh^I catalyzed isomerization of cubane into syn-tricyclo-octadiene : L. Cassar, P.E. Eaton and J. Halpern, J.Am.Chem.Soc. 92, 3515 (1970).

   b) for $Ag^\oplus$ catalyzed cubane-cuneane rearrangement : L. Cassar, P.E. Eaton and J. Halpern, J.Am.Chem.Soc. 92, 6366 (1970).

   c) for $Ag^\oplus$ catalyzed isomerization of homocubane into homocuneane : L. A. Paouette and J.S. Ward, Tetrahedron Lett. 1972, 4909.

13. N. Boder, M.J.S. Dewar and S.D. Worley, J.Am.Chem.Soc. 92, 19 (1970), report the following ΔH_f-values : norbornadiene (59.8 kcal/mole) and spiro[2.4]hepta-4.6-diene (26.2 kcal/mole). The ΔH_f value of the isomeric fulvene is comparable to the latter value.

14. This agrees with the observation that the 7-oxanorbornadiene XII -on treatment with Rh^I catalyst- isomerizes into the hydroxyfulvene IV.[2]

XII   IV