Tetrahedron Letters No. 2, pp 159 - 162, 1974. Pergamon Press. Printed in Great Britain.

MECHANISTIC DIFFERENCES BETWEEN THE Rh(I), Pd(II) AND Ag(I) CATALYZED ISOMERIZATION OF QUADRICYCLANES

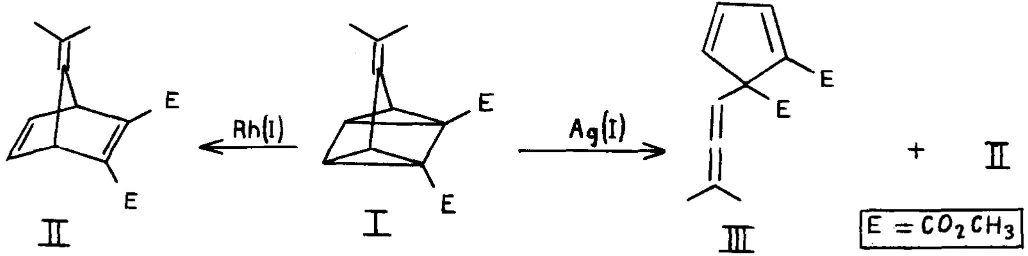
H. Hogeveen and B.J. Nusse

Department of Organic Chemistry, The University,

Zernikelaan, Groningen, The Netherlands.

(Received in UK 14 November 1973; accepted for publication 29 November 1973)

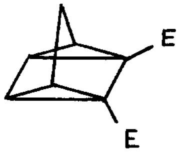
We have reported[1] that treatment of the quadricyclane I with catalytic amounts of $Rh_2(norbornadiene)_2Cl_2$ or $Rh_2(CO)_4Cl_2$ in $CHCl_3$ gives the norbornadiene II as the sole reaction product. However, Nelson, Gillespie and Hinz[2] have shown that treatment of I with catalytic amounts of $AgBF_4$ in CH_2Cl_2 affords both the cyclopentadienylallene III, as well as the norbornadiene II (30-60% and 10-20%, respectively).



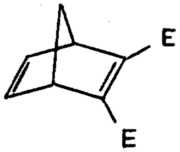
In view of these results we therefore decided to investigate the catalyst dependency of the isomerization of the quadricyclanes in greater detail. For that purpose the quadricyclane IV was chosen as substrate and $Rh_2(norbornadiene)_2Cl_2$, $Rh_2(CO)_4Cl_2$, Pd(ØCN)$_2$Cl$_2$ and $AgClO_4$ as catalysts.

Treatment of IV in aprotic solvents -$CHCl_3$ and CH_3NO_2- with these catalysts leads in all cases to the norbornadiene V as the sole product, whereas in a protic solvent -CH_3OH- the various catalysts lead to different products[3]: $Rh_2(CO)_4Cl_2$ and $Rh_2(norbornadiene)_2Cl_2$ give V and $AgClO_4$ gives the isomeric mixture VI.[4]

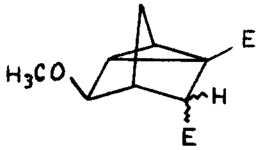
From the nature of the products formed in CH_3OH one may assume that in the case of



IV



V



VI

$AgClO_4$ an ionic mechanism obtains, in contrast to the situation with $Rh_2(CO)_4Cl_2$ and Rh_2 (norbornadiene)$_2Cl_2$. In order to understand better this divergent behaviour, we have measured the second order rate constants (See Table).

Table. Second order rate constants[a)] of the reaction: IV ⟶ V or VI

[IV]: 0,6 M [catalyst]: 0.03 M Temperature: 60°C

Catalyst	Solvent	10^2k_2 $(M^{-1}s^{-1})$
Rh_2(norbornadiene)$_2Cl_2$	$CDCl_3$	2,8[b)]
$Rh_2(CO)_4Cl_2$	$CDCl_3$	4,3
$Pd(\emptyset CN)_2Cl_2$	$CDCl_3$	4,0
$Rh_2(CO)_4Cl_2$	CD_3NO_2	43
$Pd(\emptyset CN)_2Cl_2$	CD_3NO_2	6,5
$AgClO_4$[c)]	CD_3NO_2	0,3
$Rh_2(CO)_4Cl_2$	CD_3OD	3,0
$AgClO_4$[c)]	CD_3OD	3,8

a) k_2-values for Rh(I) catalyzed reactions are composite second-order rate constants (see text).

b) this value differs by a factor of about 2 from the one previously reported,[1] which is due to the fact that the present k_2-values were determined as initial rate constants.

c) [catalyst]: 0,06 M.

From the table one observes that in chloroform the second-order rate constant of the Pd(II) catalyzed isomerization is about the same as that of the Rh(I) catalyzed isomerizations. This is difficult to reconcile with the model of Halpern, in which the oxidative addition of a quadricyclane molecule to the metal is rate determining[5], because then one would expect a lower k_2-value for the Pd(II) catalyzed isomerizations.[6] A study of the initial rates of conversion as a function of the concentration of IV, has revealed an interesting difference between the Pd(II) catalysis on one hand, and the Rh(I) catalysis on the other hand. See Figure 1.

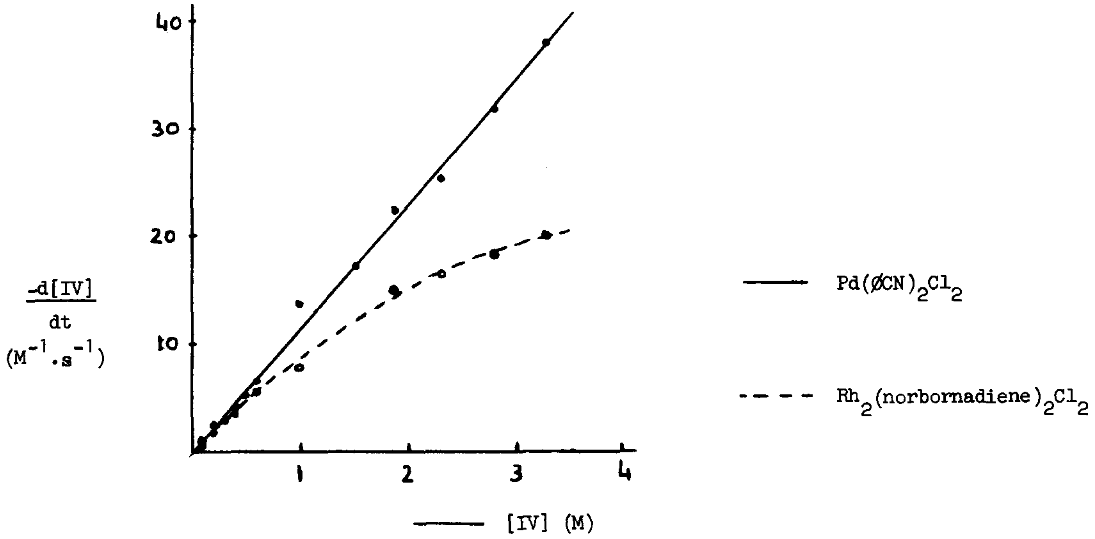


Figure 1. Initial rates of conversion IV → V as a function of [IV]; temp. 60°C; solvent $CDCl_3$.

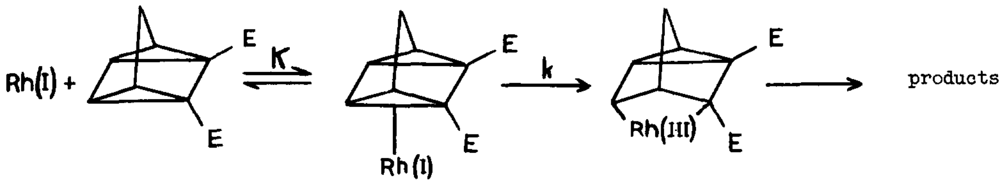
For the Pd(II) catalyzed isomerization a linear relationship is found throughout the measured concentration range (up to about 3 M). This means that one is dealing with a real second-order catalytic rate law. However, in the case of Rh(I) a deviation from linearity is observed at higher concentrations of IV. The observed relationship adheres to eq. 1, which implies the existence of a fast pre-equilibrium.[7]

$$\frac{-d[IV]}{dt} = \frac{kK[IV][Rh(I)]}{K[IV] + 1} \qquad (1)$$

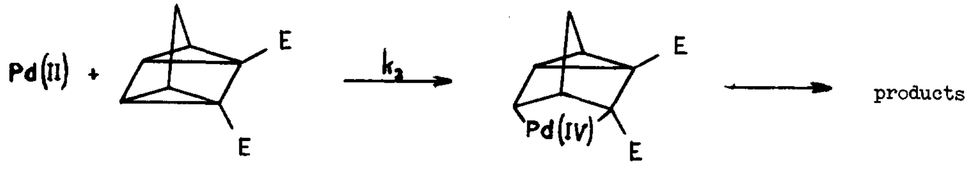
K = pre-equilibrium constant
k = rate-determing step constant

The pre-equilibrium constant was determined by the method of Lineweaver and Burk[8] and was found to be 0.32 M^{-1} at 60°C. Consistent with the model of a pre-equilibrium is the visual observation that immediately after mixing the chloroform solutions of yellow Rh_2(norbornadiene)$_2Cl_2$ with colourless substrate IV a deep red brown colour developes (without any observable isomerization of IV). At the end of the isomerization the colour is again yellow. A consequence of this pre-equilibrium is that the k_2-values of the Rh(I) catalyzed isomerizations in the Table (at least for Rh_2(norbornadiene)$_2Cl_2$ in $CDCl_3$) are not real second-order rate constants, but kK-values.

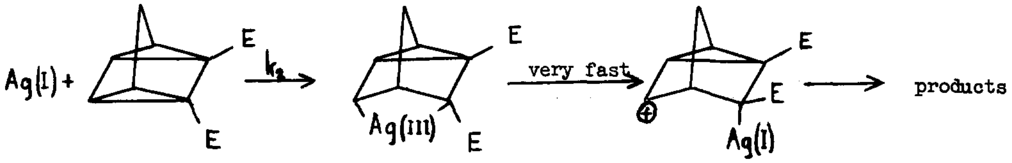
It is not clear at this moment what the precise nature of the pre-equilibrium is; possibly it involves an interaction of one cyclopropyl ring with the Rh(I) atom, so that the Rh(I) atom has become coordinately saturated.[6,9]



In the case of Pd(II) catalysis there is no such pre-equilibrium and the following scheme is suggested:



With Ag(I) catalysis the reaction scheme[10,11] (on basis of product formed in CH_3OH) can be represented as follows:



We are continuing our study in order to investigate the role of the solvent and the ligands attached to the rhodium atom.

References and notes.

1. H. Hogeveen and B.J. Nusse, Tetrahedron Lett. 1973, 3667.
2. S.F. Nelson, J.P. Gillespie and P.J. Hintz, ibid. 1971, 2361.
3. The $Pd(ØCN)_2Cl_2$ catalyzed reaction of IV in CH_3OH is complicated. Amoung the reaction products compound V is found in 40% yield together with some methanol addition products. Moreover, at the beginning of the reaction a precipitate is formed, the structure of which has not yet been determined.
4. Analogous methanol addition products were formed upon treatment of I with Ag(I) in CH_3OH.[2] The structure of the major isomer was assigned to the endo-ester on basis of NMR data, given by J.K. Stille and L.F. Hines, J.Amer.Chem.Soc. 92, 1798 (1970). Endo/exo ratio is 2 : 1.
5. L. Cassar, P.E. Eaton and J. Halpern, J.Amer.Chem.Soc. 92, 3515 (1970).
6. J.P. Collman, Acc.Chem.Res. 1, 136 (1968).
7. K.J. Laidler, "Chemical Kinetics," McGraw Hill, New York, N.Y. 1965, pp. 437-442.
8. H. Lineweaver and D. Burk, J.Amer.Chem.Soc. 56, 658 (1934).
9. Passing from Pd(II) → Rh(I) there is an increasing trend of the d^8-atom to become coordinatively saturated.[6] It is thus quite reasonable that Rh(I) becomes coordinatively saturated, whereas Pd(II) does not.
10. In this case complexation of the Ag(I) to the ester-carbonyl group constitutes another possibility.[2] This is not an oxidative addition mechanism, but it is still an ionic mechanism, which cannot be ruled out.
11. On basis of the products formed in methanol one must assume that the heterolysis of the Ag(III) complex is very much faster than the homolysis, which would lead to compound V.[12]
12. J.E. Byrd, L. Cassar, P.E. Eaton and J. Halpern, Chem.Comm. 1971, 41, state that oxidative addition to Pd(II) and Ag(I) can occur, but that the strong oxidizing character of Pd(IV) and Ag(III) promotes the heterolysis. Our observations with Pd(II) and Ag(I) are in agreement with this statement.