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Kinetics of the Isomerization of Quadricyclane to Norbornadiene Promoted by Tin(II) Chloride and Palladium(II) Chloride

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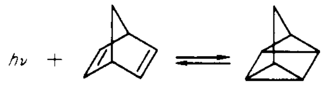
The conversion of quadricyclane to norbornadiene is promoted by both $SnCl_2$ and $PdCl_2$. The $SnCl_2$ reaction occurs by a second-order process with activation parameters of $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ of 22.5 kcal/mol, 13.9 kcal/mol, and −28.7 eu, respectively. The $PdCl_2$-promoted reaction occurs by formation of an equilibrium species and follows Michaelis–Menton kinetics. A theoretical interpretation based on the Dewar–Chatt–Duncanson model of bonding of metal ions with olefins is used to describe possible mechanistic differences in the reactions.

The norbornadiene–quadricyclane reversible isomerization is an attractive model system for solar energy storage.[1] Energy is stored when norbornadiene (**1**) is converted photochemically to the higher energy quadricyclane (**2**). The energy is released when quadricyclane is catalytically converted back to norbornadiene.

The literature contains numerous reports on the chemistry and structure of **1** and **2**,[2-4] the photochemical preparation of **2**[6] from **1**,[1g-k,5] and the catalytic conversion of **1** to **2**.[1e,6]



1 **2**

In the design of a chemical solar energy system based on valence isomerization, the photochemical reaction chamber and the catalytic conversion chamber must be kept apart. Thus, catalytic reagents that are immobilized on polymeric supports are under investigation as a means of isolating the catalytic conversion chamber.[6d,j,7] Recently we reported[7] an effective polymer-anchored stannous chloride catalyst that showed an activity for the conversion of **2** to **1** of 2 × 10^{-7} (mol Sn/L)$^{-1}$ s^{-1}. Also, King and Sweet[6d] previously reported a polymer-bound palladium(II) chloride catalyst with a kinetic activity of 0.47 (mol Pd/L)$^{-1}$ s^{-1}. Both systems suffered from loss of activity after repeated usage of the catalyst.

In an effort to design efficient reagents for the cycloreversion of **2** to **1**, we felt that a better understanding of the solution kinetics and mechanism of the reactions of the monomeric reagents was necessary. Although several reports exist on the metal-promoted conversion of **2** to **1**, only one result pertains to activation parameters, and those parameters reportedly contain large errors.[6a] Thus, we

Table I. $SnCl_2$ Isomerization Kinetic Data (CD_3OD)[a,b]

2, M	10^4k	T, K	$\Delta G^\ddagger$	$\Delta H^\ddagger_{298}$	$\Delta S^\ddagger$, eu
0.99	1.82 (0.15)[c]	298	22.5	13.9 (0.72)	−28.7
0.99	2.67 (0.15)[c]	303			
0.99	3.80 (0.37)[c]	307			
0.99	5.67 (0.41)[c]	316			
0.99	21.9 (0.22)[c]	330		ΔE_{act} = 14.5 (7.6)	
				log A = 3.74	

2, M	rate	T, K	$\Delta G^\ddagger$	$\Delta H^\ddagger_{298}$	$\Delta S^\ddagger$, eu
0.27	0.59 (0.04)[d]	298			
0.52	1.80 (0.06)[d]	298			
0.99	2.40 (0.30)[d]	298			
1.82	7.19 (0.25)[d]	298			
2.51	12.1 (0.26)[d]	298			
3.1	17.5 (0.79)[d]	298			

[a] The concentration of $SnCl_2$ is 0.29 M. Values given in parentheses are the standard deviation. All linear regression analyses provided a correlation coefficient of 0.98 or greater. [b] Activation values are in kcal/mol at 298 K. [c] In M^{-1} s^{-1}. [d] In sec.

Table II. $PdCl_2$ Isomerization Kinetic Data (CD_3OD)[a]

2, M	10^4k	T, K	$\Delta G^\ddagger$	$\Delta H^\ddagger_{298}$	$\Delta S^\ddagger$, eu
0.99	0.85 (0.06)[b]	264	21.5	5.5 (0.5)	−55.5
0.99	2.07 (0.09)[b]	273			
0.99	3.80 (0.09)[b]	299			
0.99	4.89 (0.16)[b]	311		ΔE_{act} = 6.14 (0.47)	
				log A = 1.09	

2, M	rate	T, K	$\Delta G^\ddagger$	$\Delta H^\ddagger_{298}$	$\Delta S^\ddagger$, eu
0.52	1.40 (0.08)[c]	298			
0.99	2.21 (0.09)[c]	298			
1.83	3.96 (0.11)[c]	298			
2.51	5.80 (0.13)[c]	298			
3.11	7.61 (0.11)[c]	298			

[a] $PdCl_2$ concentration is 0.29 M. See footnote at the end of Table I. [b] In M^{-1} s^{-1}. [c] In sec.

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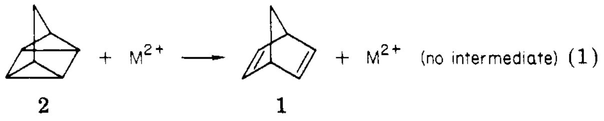
have studied the solution kinetics and activation parameters for the conversion of **2** to **1** promoted by Sn(II)Cl_2 and Pd(II)Cl_2. We report the results of our studies in this paper.

Results and Discussion

The kinetic data for the isomerization of **2** to **1** by $SnCl_2$ and $PdCl_2$ are given in Tables I and II, respectively. ^1H NMR analysis of the reactions showed clean isomerization without contamination with other byproducts.

Possible mechanisms for the conversion of **2** to **1** are shown in eq 1–3.



$$2 + M^{2+} \xrightarrow{\text{slow}} \text{complex} \xrightarrow{\text{fast}} 1 + M^{2+} \quad (2)$$

$$\begin{tikzcd} 2 + M^{2+} \arrow[r, shift left, "k"] & \text{complex} \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_2"] \arrow[d, "k_2"] & \text{intermediate} + M^{2+} \arrow[dl] \\ & 1 & \end{tikzcd} \quad (3)$$

For isomerizations of **2** to **1** promoted by $SnCl_2$, we studied the dependence of the reaction rate on quadricyclane concentration. The results given in Table I show that linear second-order kinetic behavior is followed over the entire range of concentrations of **2** studied. Both mechanisms 1 and 2 would be compatible with these results, but mechanism 3, with equilibrium formation of a complex, would require a zero-order dependence on the concentration of **2** at higher concentration according to the rate expression, rate = $V_{max}K_m(2)/(K_m + 2)$, i.e., Michaelis–Menton kinetics.[8a]

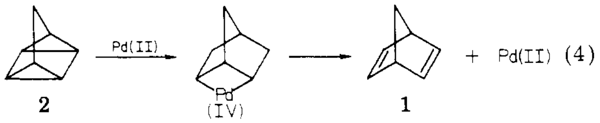
A plot of initial reaction rate against quadricyclane concentration shows upward curvature for higher quadricyclane concentrations. This result could mean that the $SnCl_2$-promoted reactions proceed through a competition of reactions 1 and 2, or that autocatalysis is involved.[8b] We have studied the ^{119}Sn NMR spectra of the isomerization reactions and we have detected a complex between Sn(II) and norbornadiene (**1**), but we have not observed any other tin complexes.

Our studies of the isomerization of **2** to **1** promoted by $PdCl_2$ permitted a clear distinction of the mechanism. Thus, the isomerizations followed linear second-order dependence of the concentration of **2** at lower concentrations, but at higher concentrations of **2**, second-order linearity was not observed. Instead, the entire range of concentrations gave a linear experimental fit with a kinetic model that describes reaction 3, Michaelis–Menton kinetics.[8a] A plot of 1/rate against 1/concentration of **2** gave a linear fit that resulted in a Michaelis–Menton constant, Km, of 7.27 M. Thus, we conclude that a complex between $PdCl_2$ and **2** is formed which can either revert to starting materials or continue to the observed reaction products.

Clearly we see that $SnCl_2$ and $PdCl_2$ follow different routes in their promotion of the isomerization of **2** to **1**. Previous kinetic studies by Hogeveen et al.[6c] have shown that equilibrium formation of a complex is involved with Rh(norbornadiene)$_2$Cl but not with Pd(PhCN)$_2$Cl$_2$. Also, Noyori et al.[6h] observed the equilibrium formation of a complex in Ni(cyclooctadiene)$_2$-promoted reactions. The involvement of equilibrium species is also well-known in the isomerization of other strained systems by metal ions, especially transition metals.

The activation parameters for our studies are given in Tables I and II. The parameters for the $PdCl_2$ reactions are taken from only one concentration of **2** and thus suffer because of the unknown dependence of the equilibrium on the temperature; the $SnCl_2$ activation parameters are, however, very reliable. The $\Delta G^{\ddagger}_{298}$ for each reaction is nearly the same with values of 22.5 kcal/mol for $SnCl_2$ and 21.5 kcal/mol for $PdCl_2$. The $PdCl_2$ reactions are, however, more driven by the entropy component ($\Delta S^{\ddagger} = -55.5$ eu) than are the $SnCl_2$ reactions ($\Delta S^{\ddagger} = -28.7$ eu). Entropy contributions are sometimes considered to indicate differences in the order of the transition state. The qualitative argument for this case would be that the values of $\Delta S^{\ddagger}$ indicate that an intermediate with greater structural order is involved in the $PdCl_2$ reactions as compared with the $SnCl_2$ reactions.

Metal-promoted isomerizations of strained hydrocarbons that involve the equilibrium formation of an intermediate species are thought to proceed by an oxidation–elimination reaction path.[1e] The path, depicted for the $PdCl_2$ reactions in eq 4, shows that Pd(II) is oxidized to Pd(IV) in A and subsequently elimination produces **1** and Pd(II). The oxidation–elimination path may be predicted with some reliability by using the Dewar–Chatt–Duncanson (DCD) model to predict the stability of the intermediates.[9]



A

The DCD model is developed for the bonding of metals to olefins but is extended to the bonding of metals to strained hydrocarbons because the strained rings (A) exhibit olefinic character. A metal ion that both donates electrons easily as determined by a low promotion energy (PI) and that accepts electrons easily as denoted through a high electron acceptor energy (EA) would be expected to form a stable complex or intermediate. Thus the low PI of 3.05 eV and the high EA of 19.42 eV for Pd(II) would lead to the prediction that Pd(II) complexes would be moderately stable, and this prediction has been borne out in numerous cases.[10] On the other hand, the values of Sn(II) of PI 11.0 (±5) eV and EA 14.6 eV indicate that Sn(II) should function as a moderately good electron acceptor (Lewis acid) but should be a poor electron donor.[11] Thus a stable complex formed through oxidation would not be expected. An intermediate such as B for $SnCl_2$-promoted isomerization of quadricyclane would thus exist only in a transitory manner as is observed in our kinetic results.

B

Conclusions

The $SnCl_2$-promoted isomerization of **2** to **1** occurs by a second-order process with possible involvement of com-

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[10] The values of PI and EA are those obtained from ref 1e.

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peting reactions or autocatalysis. The formation of a stable intermediate seems unlikely, based on the activation parameters, the ^{119}Sn NMR results, and on the DCD theoretical model.

Isomerization of **2** to **1** by $PdCl_2$ occurs at a slower rate than the $SnCl_2$ reaction but both reactions have nearly the same $\Delta G^\ddagger$ values. Thus $PdCl_2$ reaction rates are slower because of the zero-order dependence of the reaction at higher concentrations of quadricyclane. These results are compatable with the reversible formation of an intermediate species.

Experimental Section

All materials used were obtained from commercial sources and were not purified: deuterated methanol (Sigma), quadricyclane (Aldrich), stannous chloride (Fischer), palladium chloride (Alfa), *p*-dichlorbenzene (Fischer). ^{1}H NMR spectra were recorded at 60 MHz on a JEOL-FX60Q pulsed NMR spectrometer. A spectral with width of 600 Hz was used with a single 90° pulse and 8K bits of data collection. Probe temperatures were measured with a thermometer immersed in a sample tube placed in the NMR cavity before and after each run.

Kinetic Experiments. A solution consisting of 1.0 mL of CD_3OD, an accurately measured amount of quadricyclane, and 50 mg of *p*-dichlorobenzene (which was used as an internal standard for proton integration) was placed in the NMR instrument probe and the instrument was tuned to 0.15-Hz resolution. $SnCl_2$ (50 mg) or $PdCl_2$ (50 mg) was added all at once to the tube, the contents were shaken vigorously, and the sample was locked on the deuterium signal of the spectrometer.

Spectra were recorded and stored on tape at 2–5-min intervals for a period of 2–4 h. The amount of norboradiene produced was obtained from NMR integration of the four-proton alkene multiplet at 6.8 ppm and referenced to the four-proton singlet for *p*-dichlorobenzene at 7.1 ppm. The relative integrated area obtained for norbornadiene was used in a second-order plot of $(\ln 1/(a - b))(\ln (b(a - x)/a(b - x)))$ vs. time (s), where a and b are the initial molar concentrations of metal salt and quadricyclane, respectively, and x is the molar concentration of norbornadiene formed. First-order plots exhibited linearity in some cases, but second-order kinetics were consistently much better as determined from linear least-squares correlation coefficients of 0.98 or greater and standard deviation of less than 3%.

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Registry No. $SnCl_2$, 7772-99-8; $PdCl_2$, 7647-10-1; quadricyclane, 278-06-8; norbornadiene, 121-46-0.

Stereo- and Photochemistry of 1,2,3,4,5-Pentaphenyl-1,3,5-heptatriene

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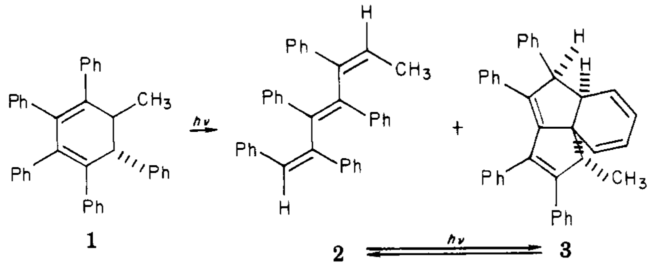
The stereochemistry of 1,2,3,4,5-pentaphenyl-1,3,5-heptatriene (**2**) previously isolated from the photolysis of *cis*-6-methyl-1,2,3,4,5-pentaphenyl-1,3-cyclohexadiene has been shown to be *Z,E,Z* on the basis of X-ray crystallographic analysis and chemical data. The stereo- and regiospecificity of the formation and further photolysis of **2** to a tricyclo photoproduct by an apparent [6 + 2] cycloaddition reaction are discussed.

Introduction

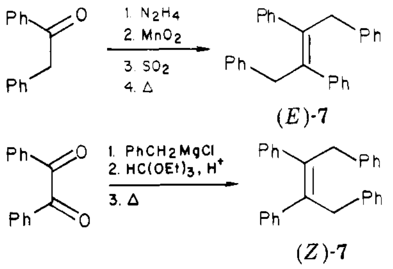
Irradiation of 6-methyl-1,2,3,4,5-pentaphenyl-1,3-cyclohexadiene (**1**) has been previously shown to generate the tricyclo[6.4.0.0^{4,8}]dodecatetraene **3** as well as an open chain triene **2** (reaction 1).[1] Evidence has also been presented



(1)

supporting the generation of **3** from **2** in the photolysis mixture.[1] On the basis of the unifying concept of cyclohexadiene–hexatriene photochemistry that the principle ground-state conformation of the polyene would determine the reaction path for the triene,[2-5] we contended that the

Scheme I



lack of ground-state conformers allowing either vinylcyclobutene or bicyclo[3.1.0]hexene formation forced another reaction path on triene **2**, a [6 + 2] cycloaddition reaction to tricyclo **3**. In order to investigate this possiblity further, a determination of the stereochemistry and ultimately the conformation of the triene **2** was initiated, using chemical as well as crystallographic analysis. This report validates aspects of the contention mentioned above.

Results

Initially it was felt that the stereochemistry of triene **2** could be established by comparison to a series of models

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