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PALLADIUM(0) CATALYZED REACTION OF 1,3-DIENE 1,4-EPIPEROXIDES

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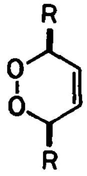
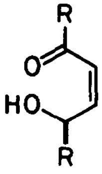
Summary: Reaction of 1,3-diene 1,4-epiperoxides with $Pd(PPh_3)_4$ catalyst forms the corresponding 4-hydroxy enones, syn diepoxides, and 1,4-diols as the major products. The results are interpreted as being due to competing Pd(0)/Pd(II) and Pd(0)/Pd(I) exchange mechanisms.

The transition metal catalysis of unsaturated 1,4-epiperoxides (endoperoxides) of type I has been examined with Fe(II),[1] Ti(III),[2] Co(II),[3] and Rh(I)[4] salts or complexes. In connection with our recent project on the site-selective oxygenation of unsaturated organic frameworks,[5,6] we have investigated the behavior of I in the presence of a Pd(0) complex.[7]

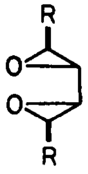
When an epiperoxide I in dichloromethane was exposed to 5—10 mol % of $Pd(PPh_3)_4$, the O—O bond was cleaved to give the products of type II—IV. Both monocyclic and bicyclic substrates are susceptible to the redox catalysis under the homogeneous, neutral conditions. The relative reactivities and importance of the reaction pathways are affected by the ring systems. The results obtained with a series of unsaturated epiperoxides are listed in Table I. 4-Hydroxy-2-cyclopentenone thus formed (entry 1) serves as an important prostaglandin synthetic intermediate.[8,9] Certain hydroxy enone products of type II, particularly those derived from the monocyclic substrates, underwent further reaction to form the more stable E isomer, 1,4-diketone, hemiacetal, or furan derivatives (entry 9—12).



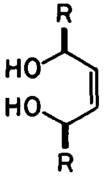
I



II



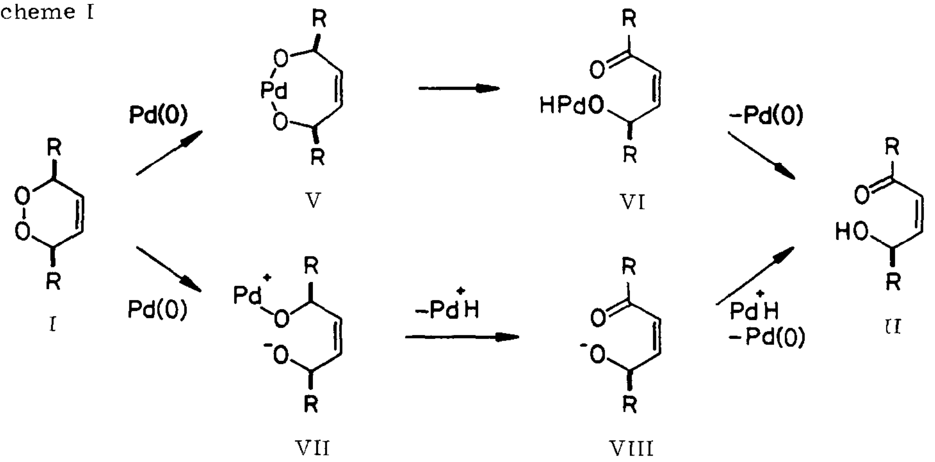
III



IV

The epiperoxide to hydroxy enone conversion, I → II, is best interpreted in terms of the Pd(0)/Pd(II) exchange mechanism as outlined in Scheme I. Oxidative addition of the O—O bond of I to the zerovalent Pd atom produces the cyclic structure V.[10] Subsequent β-elimination of a PdH element, giving VI, followed by reductive elimination of Pd(0)

Scheme I



species leads ultimately to the hydroxy enone II. Alternatively, the initial attack of Pd(0) species to an oxygen atom of I in an S_N2 manner[11] also cleaves the O—O linkage to generate the zwitterion VII. Subsequent hydrogen reorganization via PdH species formed by β-elimination results in the same product II.

Apparently the catalytic isomerization of I to the syn diepoxide III and the production of the 1,4-diol IV result from some radical processes.[1—3] Although Pd complexes have a trend to cause reactions via two-electron redox mechanism, it is tempting to assume a Pd(0)/Pd(I) exchange mechanism for these transformations (Scheme II).[12] Thus the radical intermediate IX could be produced by direct Pd atom transfer to I or via prior one-electron transfer. The interaction of the oxy radical with the internal double bond leads to the

Scheme II

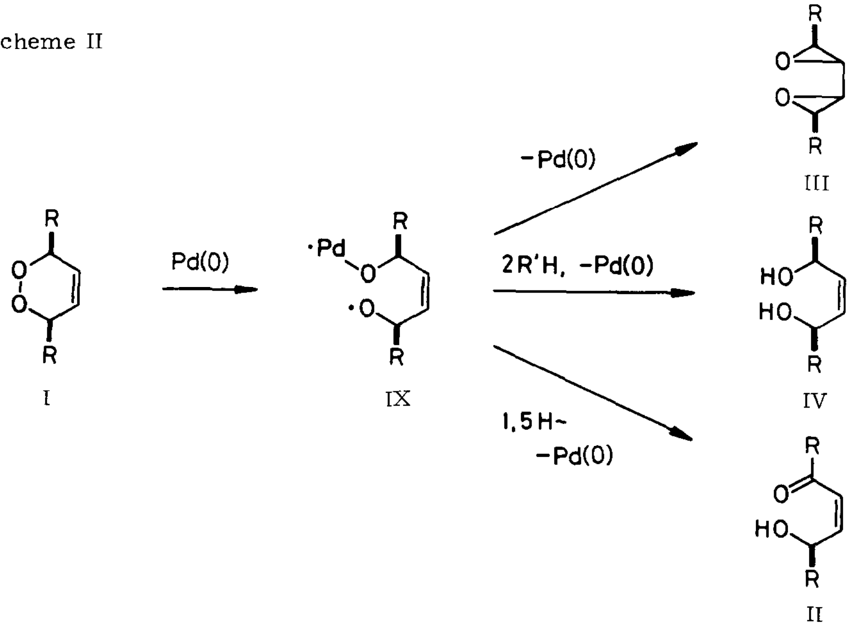
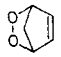
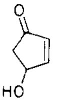
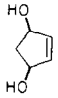
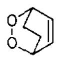
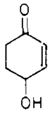
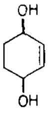
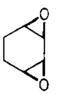
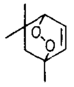
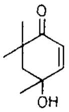
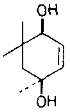
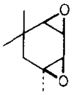
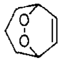
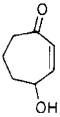
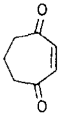
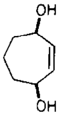
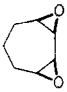
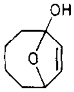
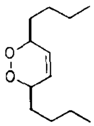
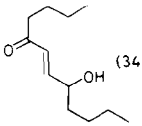
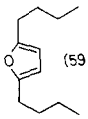
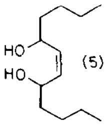
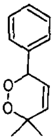
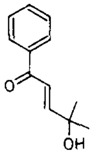
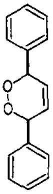
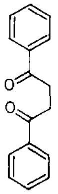


Table I. Palladium(0) Catalyzed Reaction of 1,3-Diene 1,4-Epiperoxides[a]

		conditions						
entry	epi-peroxide	catalyst mol %	temp °C	time h	product (% yield)[b]			
1		10	4^c	20	 (54)	 (16)^d		
2		5	50-60	5	 (39)	 (30)	 (8)^e	
3		5	50-60^f	5	(42)	(32)	(9)^e	
4		5	50-60^g	5	(39)	(50)	(6)^e	
5	 ^{h}	5	60	46	 (68)^h	 (6)^h	 (24)^h	
6		5	60	29	 (40)^h	 (3)	 (19)	 (24)^e
7		10	60	29	(45)	(10)	(17)	(28)^e
8		10	60^f	29	(44)	(9)	(17)	(29)^e
9		5^i	60	29	 (51)			
10	 ^{h}	5	60	39	 (34)^h	 (59)	 (5)^h	
11	 ^{h}	5	100	15	 (66)^h			
12		6	70	12	 (74)^d			

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[a] Unless otherwise stated, the reaction was carried out in dichloromethane under argon atmosphere by using $Pd(PPh_3)_4$ as catalyst. [b] Isolated yield. [c] The catalyst and substrate were mixed at -78 °C. [d] Analyzed by ^{1}H NMR. [e] Analyzed by GLC. [f] Five mol % of 2,4,6-tri-t-butylphenol was present. [g] Ten equiv of 2-propanol was added. [h] A new compound giving correct elemental analysis. [i] Benzene was used as solvent.

diepoxide III, whereas the abstraction of hydrogen atoms from the donors present in the reaction system provides the 1,4-diol IV. Since secondary alcohols serve as a good hydrogen donor,[13] the initially formed alcoholic products would be converted partly to the ketonic derivatives. The oxy radical IX possessing a flexible structure may undergo intramolecular 1,5-hydrogen abstraction[1c] to form II, consistent with the no or little production of III or IV in the reaction of monocyclic epiperoxide substrates (entry 10—12). A radical chain mechanism, however, is unlikely to be operative, because addition of 5 mol % of 2,4,6-tri-*t*-butylphenol did not affect to any significant extent the reaction of 3,7-epiperoxycycloheptene (entry 8).[14]

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13. The reaction of I (R—R = (CH$_2$)$_2$) in the presence of 10 equiv of 2-propanol produced acetone in 20% yield. The yield of the 1,4-diols increased to some extent (entry 4).
14. Throughout the reaction no appreciable decomposition of the Pd catalyst took place; neither Pd mirror nor insoluble precipitates were formed. Pd(PPh$_3$)$_4$ is known to dissociate to Pd(PPh$_3$)$_n$ (n = 3 or 2) and PPh$_3$ in solution. When a 1:1 mixture of I (R—R = (CH$_2$)$_3$) and PPh$_3$ in CH$_2$Cl$_2$ was heated at 60 °C for 6 h, 1,2-epoxy-3-cycloheptene was obtained as a sole product in 100% yield (90% conversion). The coordinatively unsaturated Pd(0) species is much more reactive than PPh$_3$ and, under the catalysis conditions, only Pd(0) reacts with the epiperoxide substrates.

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