

EPOXIDATION WITH O₂ USING PdClNO₂(CH₃CN)₂ CATALYSTS:
REACTIVITY OF THE C-Pd BOND IN THE INTERMEDIATE
COMPLEX FORMED DURING OXIDATION OF NORBORNENE

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Abstract: The reactivity of di- μ -chlorobis[3-(nitrosooxy)bicyclo[2.2.1]hept-2-yl-C,N] dipalladium II can be modified by added reagents. In presence of CuCl₂, the thermal decomposition leading to epoxy-norbornane is completely suppressed and an unequivocal rearrangement of the norbornane framework is observed.

We have previously shown (1a) that strained olefins like vinyl-norbornene can be selectively epoxidized by direct oxidation with molecular oxygen catalyzed by PdCl(NO₂)(RCN)₂ I (2). This epoxidation reaction suffers from two drawbacks: low turn-overs which are likely to be due to the difficulties of regenerating the catalytic species I from the (PdClNO)_n polymer formed in the catalytic cycle, and limitation (as far as the epoxide selectivity is concerned) to the norbornene type double bond. In order to improve this reaction, we have studied the influence of R in I. By changing R (=nPr), the turn-over could be increased from 3 to 9 (chemical yield 63%) but nevertheless remains low. In the present paper (3), we report our results concerning the reactivity towards CuCl₂ of the isolated complex II (1b) formed from norbornene and I (see table 1).

The aim of this work was to obtain a better knowledge of the reactivity of the C-Pd bond (4) as compared to other metals (5). Our ultimate goal was to achieve an exclusive attack of the oxygen of II on the carbon bearing the palladium, which would be independent of the peculiar features of the norbornane skeleton.

The reaction products (6) have been separated (liquid chromatography on

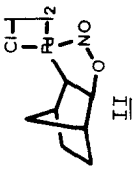


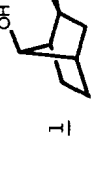


ENTRY	SUBSTRATE	REACTION CONDITIONS	YIELD	PRODUCTS COMPOSITION
1		2 CuCl ₂ , 24 hrs CH ₃ CN	77%	 85.1%  4.9%  7.5% 23.0% 6.4%
2	"	2 CuCl ₂ , 5 LiCl CH ₃ CN, 24 hrs	57%	91.5% 4.5% 1.6%
3	"	2 CuCl ₂ , 5 LiOAc CH ₃ CN, 24 hrs	62%	traces
4		2 CuCl ₂ , 6 Days CH ₃ CN	--	traces
5		2 CuCl ₂ , 5 LiOAc CH ₃ CN, 24 hrs	--	3.0% 4.5% -- (4 unchanged 91.0%)

Table 1: Reaction of complex II with CuCl₂ (6)

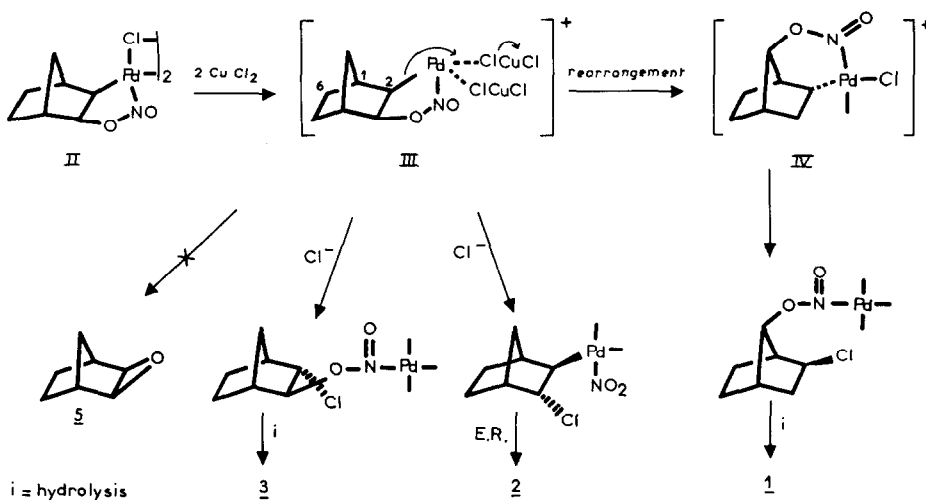
a) IR(HCCl₃): 1550 (νNO₂asy.), 1373 (νNO₂sy.) cm⁻¹

¹H NMR (CDCl₃): δ(ppm) 4.80, b.s., H₂endo (H-CNO₂)
4.30, d. of d., H₃exo (H-C₁Cl), J_{2,3}trans=2.0Hz, J_{4,3}exo=3.6Hz
bridgedhead protons:
2.89, d., H₄, J_{4,3}exo=3.6Hz
2.62, b.s., H₁

GC-MS m/e: 30 (19.4% NO⁺), 39 (100%), 41 (64.3%), 46 (8.7% NO₂⁺), 129 (48.3%, C₇H₁₀³⁵Cl(M-NO₂)),
131 (14.3%, C₇H₁₀³⁷Cl(M-NO₂)).

Kieselgel 60) and identified by IR, ^1H and ^{13}C NMR, GCMS and for 1 and 3 by comparison with authentic samples (7,8). Epoxide 5 which is not detected in the reaction products, reacts only very slowly in these conditions (entry 4).

These results are complementary to those of Mares (3b) who is studying the reactivity of similar acyclic palladium nitro complexes which yield glycol acetates. The most striking feature of our reaction is the obtention of the rearranged product 1 comparable to the one previously obtained (9) by treatment of norbornene with PdCl_2 and CuCl_2 in acetic acid.



The addition of CuCl_2 to the complex II (10) forms complex III which undergoes a rearrangement. The latter does not occur on norbornene which is not reactive under these conditions (entry 5) (11). The leaving properties of the Pd group in III are then perfectly adapted to the migratory aptitude of the C6-Cl bond, thus leading to the formation of complex IV giving 1.

Another interesting observation results from the fact that even in presence of an excess of LiOAc (see entry 3) no acetoxyated products are formed. Normally a nucleophilic attack of the acetate anion - which is

observed when II is acetolyzed- is likely to be due to the difficulty of endo attack on the norbornane skeleton (12) and to the non appropriate softness of the acetate oxygen (13).

The present results show that the C-Pd bond reactivity can be modified by changing the ligands around the palladium in complexes such as II. It is therefore reasonable to expect to achieve in a much more general way, independent of the norbornene system, an exclusive and efficient attack of the oxygen on the carbon bearing the palladium (epoxidation).

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- 6- In a typical experiment, reagents CuCl_2 (269 mg) and LiX (X=Cl 212 mg, OAc 330 mg)- ratioPd:Cu:Li=1:2:5- were added to a solution of 0.5 mMole (282 mg) of II in 20 mL. of dry CH_3CN . The mixture was stirred 24 hours at 25°C and then hydrolyzed with 10 mL. of H_2O . The products were extracted with Et_2O (3x5 mL.) and the organic solution washed with brine (2x10mL.), dried over MgSO_4 and evaporated under vacuum .
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