

Formation of Condensed Tetrahydrofurans in the Oxidation of Norbornene by Bis(acetonitrile)chloronitropalladium(II)

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The $(\text{MeCN})_2\text{PdCl}(\text{NO}_2)$ -catalysed air oxidation of norbornene gives nearly exclusively *exo*-epoxynorbornene at low norbornene concentrations but predominantly condensed tetrahydrofurans derived from two norbornene units and one oxygen atom at high norbornene concentrations.

The transition metal nitro-nitrosyl redox couple-catalysed air oxidation of alkenes has been reported to proceed *via* oxygen transfer from the nitro ligand to the organic substrate to give either ketones or epoxides with high selectivity.¹⁻⁵ We report here that in the $(\text{MeCN})_2\text{PdCl}(\text{NO}_2)$ (1)-catalysed air oxidation of norbornene, dimerization can occur in concert with oxygen transfer to form tetrahydrofurans consisting of two norbornene units and one oxygen atom.

The (1)-catalysed air oxidation of norbornene has been reported to proceed *via* the isolable heterometallacyclopentane (2) to give *exo*-epoxynorbornene (3) with >99% selectivity.⁴ However, we find the selectivity to be strongly dependent on norbornene concentration as shown by the results in Table 1. The epoxide (3) was formed at >94% selectivity at very low norbornene concentrations (Table 1, entries 1 and 6). At high norbornene concentrations, a condensed tetrahydrofuran (4) and small amounts of its isomers were the major organic products. The isomeric selectivity for formation of (4) was >90%. The crude product (4) was isolated as a white solid

with a melting range of 44–50 °C. No attempts were made to study the possible interconversion between (4) and its isomers.

The structure of (4) was elucidated using mass and n.m.r. spectroscopy as follows. The molecular weight was determined to be 204 and with the reported intermediacy of (2),⁴ a condensed tetrahydrofuran derived from one oxygen and two norbornene units was proposed. This was confirmed by ¹³C n.m.r. spectroscopy which showed a symmetrical structure since there were only seven distinct carbons (four methines and three methylenes). A chiral shift reagent (Regis P64-178-1) was used to demonstrate that (4) is chiral and therefore the two norbornene units are *anti*. A complete two-dimensional ¹H n.m.r. analysis showed that the norbornene units are substituted in the *exo* positions (Figure 1).

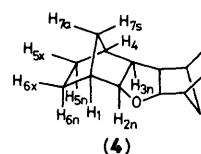
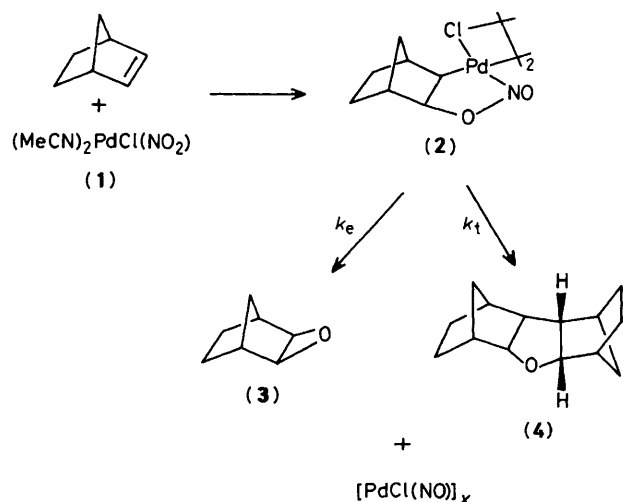


Table 1. $(\text{MeCN})_2\text{PdCl}(\text{NO}_2)$ -catalysed air oxidation of norbornene.

Entry	Solvent	T/°C	[Norbornene]/M	f_e^a	Turnover no. ^b
1	Toluene	25	0.04	0.94	0.55
2	Toluene	25	1	0.11	5.3
3	Toluene	25	2	0.06	4.9
4	Toluene	25	4	0.03	4.4
5	EtOAc	60	4	0.02	4.2
6	EtOAc	60	0.04	0.98	7.3

^a Mole fraction of epoxide (3) in organic products after 24 h. ^b Based on palladium.



Scheme 1

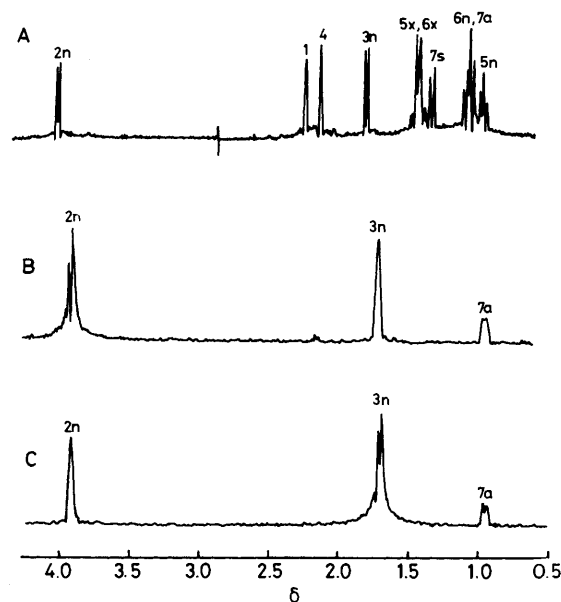


Figure 1. (A) 360 MHz ¹H n.m.r. spectrum ($\text{C}_2\text{D}_2\text{Cl}_4$) of (4). Resonances were assigned using the two-dimensional technique of spin-echo correlated spectroscopy (SECSY); by taking cross sections through peaks in the SECSY spectrum the *J*-coupling network may be quickly elucidated: δ 3.92 (1H, m, $J_{2,3}$ 6.1 Hz), 2.15 (1H, br.s), 2.05 (1H, br.s), 1.72 (1H, m, $J_{2,3}$ 6.1 Hz), 1.35 (2H, m), 1.25 (1H, m, $J_{7a,7s}$ 10.1 Hz), 1.00 (1H, m), 0.96 (1H, m, $J_{7a,7s}$ 10.1 Hz), and 0.88 (1H, m). (B) A cross section through the 2n peak reveals coupling to 3n and 7a. (C) A cross section through 3n reveals coupling to 2n and 7a. The *W*-coupling of 2,3 to 7a was used to assign the *exo,exo* configuration.

Compound (4) is specified therefore as the symmetrical *exo*, *anti* isomer.

The dependence of product selectivity on norbornene concentration is consistent with two competing catalytic cycles sharing a common intermediate (2), as shown in Scheme 1. This is supported by the reaction of (2) with norbornene in N₂ to afford (4) in 35% yield. The possibility of a [PdCl(NO)]_x-induced coupling of the epoxide (3) and norbornene to yield (4) may be ruled out by the lack of reaction between (3), [PdCl(NO)]_x, and norbornene in N₂. The formation of (4) probably proceeds by a *cis-anti* insertion of norbornene into the Pd-C σ-bond in (2) followed by reductive elimination with retention of configuration at the carbon atom.

It can be readily derived from Scheme 1 that at low conversions, the mole fraction of (3), f_e , in the organic products can be described by the equation $1/f_e = 1 + (k_t/k_e)$

k_t/k_e estimated to be *ca.* 8 in toluene at 25 °C from a plot of $1/f_e$ vs. [norbornene].

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References

- 1 B. S. Tovrog, F. Mares, and S. E. Diamond, *J. Am. Chem. Soc.*, 1980, **102**, 6616.
 - 2 M. A. Andrews and K. P. Kelly, *J. Am. Chem. Soc.*, 1981, **103**, 2894.
 - 3 S. E. Diamond, F. Mares, and S. Szalkiewicz, *J. Am. Chem. Soc.*, 1982, **104**, 4266.
 - 4 M. A. Andrews and C. W. F. Cheng, *J. Am. Chem. Soc.*, 1982, **104**, 4268.
 - 5 A. Heumann, F. Chauvet, and B. Waegell, *Tetrahedron Lett.*, 1982, **23**, 2767.
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