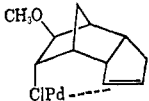
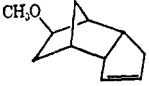




Table I. Reductions in Dry Monoglyme<sup>a</sup>

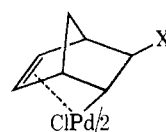
Starting complex	Trap (moles)	Overall yield, <sup>b</sup> %	Products (rel yield, %)
Ia	Norbornene (20)	70	IIIa (84), dihydro-IIIa (5), IVa (11)
Ia	Norbornene (2)	80	IIIa (34), dihydro-IIIa (64), IVa (2)
Ia	2,3-Dicarbomethoxy-norborn-5-ene (20)	76	IIIa (37), dihydro-IIIa (57.5), IVa (2), norbornene (2), norbornane (1), norbornadiene (0.5)
Ib <sup>c</sup>	Norbornene (20)	64	IIIb (89), dihydro-IIIb (8), IVb (3)
IIb	Norbornene (20)	85	IIIb (2), dihydro-IIIb (1), IVb (97)
IIa	Norbornene (20)	80	IVa (100)
IIc	Norbornene (20)	82	IIIa (1), dihydro-IIIa (1), IVa (98)
	Norbornene (20)	67	 (98), dicyclopentadiene (1), dihydrodicyclopentadiene (1)

<sup>a</sup> 3 hr at  $-40^\circ$ ; 1:1  $\text{NaBH}_4$  ( $\text{NaBD}_4$ ):Pd. <sup>b</sup> Yields by glpc; hydrocarbon products could not be determined from I or II in experiments using norbornene. <sup>c</sup> Reference 2c.

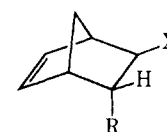
olysis of oxygen substituents.<sup>3</sup> We have found that both of these side reactions can be suppressed by excess norbornene in monoglyme at  $-40^\circ$ . The function of norbornene is most likely to trap diborane,<sup>4</sup> produced *in situ* by the reaction  $\text{RPdCl} + \text{NaBH}_4 \rightarrow \text{RPdH} + \text{NaCl} + [\text{BH}_3]$ . While saturated hydrocarbons are major products in the absence of norbornene, our conditions permit specific reduction at palladium-carbon  $\sigma$  bonds in a variety of palladium complexes (Table I). Thus, acetoxy complexes Ia<sup>5</sup> and IIa<sup>6</sup> are reduced to the corresponding acetates IIIa and IVa in good yield.

The small proportion of rearranged product IVa from reduction of Ia is probably the result of conversion of Ia to IId by norbornene. Other coordinating agents such as pyridine,<sup>6</sup> bis(diphenylphosphino)ethane,<sup>7a</sup> and carbon monoxide<sup>7b</sup> are known to induce closure of Ia or Ib to the corresponding tricyclic structures. In the present case, norbornene may induce some closure of Ia prior to reduction. A decrease in the norbornene:Ia ratio from 20:1 to 2:1 causes a decrease in the relative yield of rearranged acetate IVa from 11 to 2%, but diborane is no longer trapped as effectively and overreduction products predominate (Table I, entry 2). The minor rearranged products

(<3%) from reduction of IIb or IIc can be explained similarly since the equilibrium between IIb or IIc and bicyclic complex + pyridine can be observed by nmr.<sup>6</sup> This equilibrium is not operative with the strongly co-



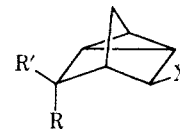
Ia, X = OAc  
b, X = OCH<sub>3</sub>



IIIa, R = D; X = OAc  
b, R = H; X = OCH<sub>3</sub>



IIa, X = OAc; L<sub>2</sub> =  $(\text{Ph}_2\text{PCH}_2)_2$   
b, X = OCH<sub>3</sub>; L = pyridine  
c, X = OAc; L = pyridine  
d, X = OAc; L = norbornene



IVa, X = OAc; R' = H; R = D  
b, X = OCH<sub>3</sub>; R = R' = H

ordinated complex IIa,<sup>6</sup> and acetoxy-norbornene (IVa) is the sole reduction product.

The stereochemistry of deuterium in *exo*-2-acetoxy-norborn-5-ene (IIIa) was proved by comparison of spectra with IIIa as prepared by Berson and Nelson.<sup>8</sup> Partial overlapping of the nmr signals from H<sub>3</sub> endo and H<sub>7</sub> prevented an accurate analysis of deuterium content, so the acetate IIIa was converted to *exo*-2-norbornenol with lithium aluminum hydride. The necessary nmr signals of *exo*-2-norbornenol can be resolved cleanly in the presence of tris(dipivaloylmethanato)europium,  $\text{Eu}(\text{DPM})_3$ ,<sup>9</sup> and the spectrum is reproduced in Figure 1, trace A. Careful integration reveals that all of the deuterium, within limits of integral accuracy, is located at the 3-endo position of the *exo*-2-norbornenol derived from IIIa.

Similarly, IVa was converted to Va by known methods and the nmr spectrum of the latter was examined in the presence of  $\text{Eu}(\text{DPM})_3$ . At a ratio of 0.22 mol of europium/mol of V, the chemical shifts of H<sub>b</sub> and H<sub>c</sub> become identical, and the complex cyclopropyl signals collapse to a broad singlet. Integration

(8) J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968); J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **89**, 5503 (1967).

(9) J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970).

(3) (a) J. K. Stille and R. A. Morgan, *J. Amer. Chem. Soc.*, **88**, 5135 (1966); (b) C. B. Anderson and B. J. Burrenson, *J. Organometal. Chem.*, **7**, 181 (1967).

(4) We have found that reduction of palladium complexes with diborane in THF produces hydrocarbons directly, presumably *via* palladium hydrides. The mechanism of deoxygenation remains obscure; acid-catalyzed deoxymetalation has been suggested as a possible first step.<sup>3a</sup>

(5) Ia was prepared by the method of Anderson and Burrenson:<sup>3b</sup> pale yellow crystals from benzene-hexane; 140–180° dec (sealed capillary); mol wt (benzene) 603 (calcd 586). The bicyclic structure is indicated by the presence of two olefinic protons at  $\delta$  6.0–6.2 in the nmr spectrum ( $\text{CDCl}_3$ ).

(6) IIa was prepared by the method of Coulson:<sup>7a</sup> mp 245, 165° dec; nmr ( $\text{CDCl}_3$ )  $\delta$  0.62 (1 H, t,  $J = 5$  Hz), 0.7–2.9 (10 H, m), 1.92 (3 H, s), 5.08 (1 H, br s), 7.25–8.15 (20 H, m). IIb has been prepared previously by Green and Hancock,<sup>2c</sup> but the structure was assigned incorrectly as bicyclic  $\text{C}_7\text{H}_8(\text{OCH}_3)\text{Pd}(\text{C}_5\text{H}_5\text{N})_2^+\text{Cl}^-$ . The nmr spectrum of IIb (or IIc, prepared similarly) requires the tricyclic structure: IIb, mp 123.5–124.5° dec; mol wt (benzene) 428, calcd 423; nmr ( $\text{CDCl}_3 + 10\%$  pyridine);  $\delta$  0.35 (1 H, t,  $J = 5$  Hz), 0.9–1.7 (5 H, m), 2.08 (1 H, br s), 3.16 (3 H, s), 4.49 (1 H, br s), 7.35 (4 H, m), 7.78 (2 H, m), 8.92 (4 H, m). In  $\text{CDCl}_3$  without added pyridine, the above signals accounted for 85% of the spectrum, and new signals appeared at  $\delta$  5.8–6.2 (m), 3.3 (s), 4.15 (br s), and 8.5 (m), indicating 15% bicyclic complex and free pyridine in equilibrium with IIb. Similarly IIc was prepared from Ia and pyridine: mp 116–118° dec; mol wt (benzene) 477, calcd 451. The nmr spectrum of IIc is analogous to that of IIb, and also indicates 15% bicyclic complex in  $\text{CDCl}_3$  without excess pyridine added.

(7) (a) D. R. Coulson, *J. Amer. Chem. Soc.*, **91**, 200 (1969); (b) J. K. Stille and L. F. Hines, *ibid.*, **92**, 1798 (1970).

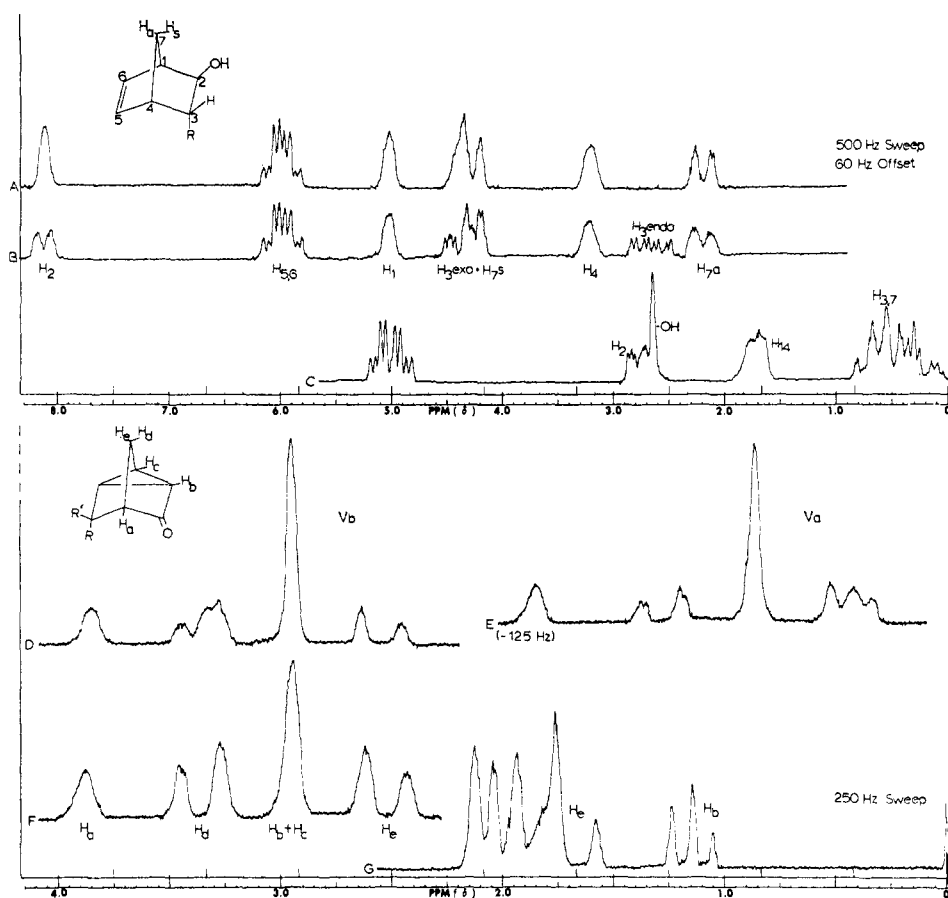
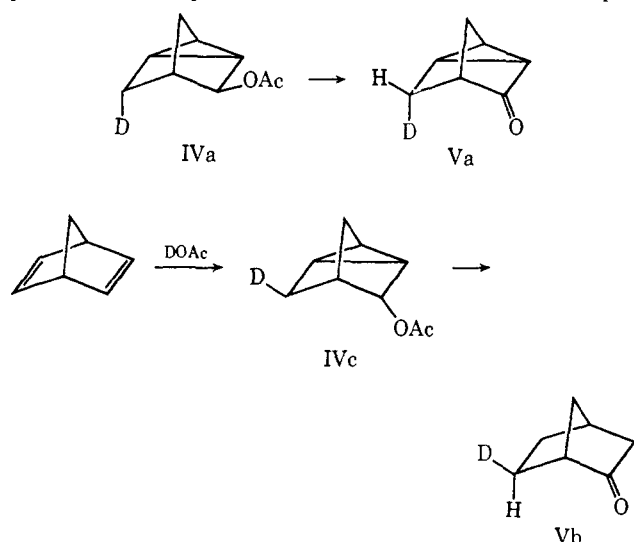


Figure 1. *exo*-Norbornenol: trace A, R = D; 22 mol % Eu(DPM)<sub>3</sub>-CCl<sub>4</sub>; B, R = H; 22 mol % Eu(DPM)<sub>3</sub>-CCl<sub>4</sub>; C, R = H; CCl<sub>4</sub>. Nortricyclenone: trace D (Vb), R<sup>1</sup> = D; R = H; 22 mol % Eu(DPM)<sub>3</sub>-CCl<sub>4</sub>; E (Va), R<sup>1</sup> = H; R = D; 22 mol % Eu(DPM)<sub>3</sub>-CCl<sub>4</sub>; F, R<sup>1</sup> = R = H; 22 mol % Eu(DPM)<sub>3</sub>-CCl<sub>4</sub>; G, R<sup>1</sup> = R = H; CCl<sub>4</sub>.

of the resulting spectrum (Figure 1, trace E) shows that deuterium in Va is located exclusively at the 5-endo position. The isomeric 5-exo deuterated ketone Vb was prepared from the known acetate IVc,<sup>10</sup> and comparison of the spectra of Va and Vb confirms our spec-



tral and stereochemical assignments.<sup>11</sup>

(10) S. J. Cristol, T. C. Morill, and R. A. Sanchez, *J. Org. Chem.*, **31**, 2719 (1966), and references therein.

(11) Mass spectral analysis indicates the following distribution of deuterium, confirmed by nmr integration: IIIa, 7% d<sub>0</sub>, 92% d<sub>1</sub>, 1% d<sub>2</sub>; Va, 9.5% d<sub>0</sub>, 90% d<sub>1</sub>, 0.5% d<sub>2</sub>; Vb, 6.5% d<sub>0</sub>, 92% d<sub>1</sub>, 1.5% d<sub>2</sub>. The

Both Ia and IIa are reduced by sodium borodeuteride with >97% retention of stereochemistry<sup>12</sup> and structure. The high specificity of reduction is inconsistent with a mechanism involving long-lived radical intermediates, as proposed for reduction of the mercury analogs of I and II.<sup>1</sup> Our results are consistent with an alternate interpretation involving initial formation of RPdH followed by concerted collapse to RH and palladium metal.<sup>13</sup>

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per cent d<sub>0</sub> species corresponds to the isotopic distribution of the commercial deuterated reagents NaBD<sub>4</sub> and DOAc used in our work.

(12) Predominant retention of stereochemistry (per cent unspecified) has also been observed in the reduction of methoxydicyclopentadienyl-palladium chloride dimer by Stille and Morgan.<sup>3a</sup>

(13) A nonradical bimolecular mechanism is also conceivable, and has some analogy: G. M. Whitesides, J. San Filippo, Jr., E. R. Stredronsky, and C. P. Casey, *J. Amer. Chem. Soc.*, **91**, 6542 (1969).

\* Address correspondence to this author.

Edwin Vedejs,\* Mary F. Salomon  
Department of Chemistry, University of Wisconsin  
Madison, Wisconsin 53706  
Received August 24, 1970

### Exchange of Olefins with Oxymercurials

Sir:

We have found that oxymercurial ions (abbreviated Hg(OI)OH<sup>+</sup>), formed by reactions of olefins with mer-