

## Palladium-Catalyzed Vinylation of Conjugated Dienes

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Received September 12, 1978

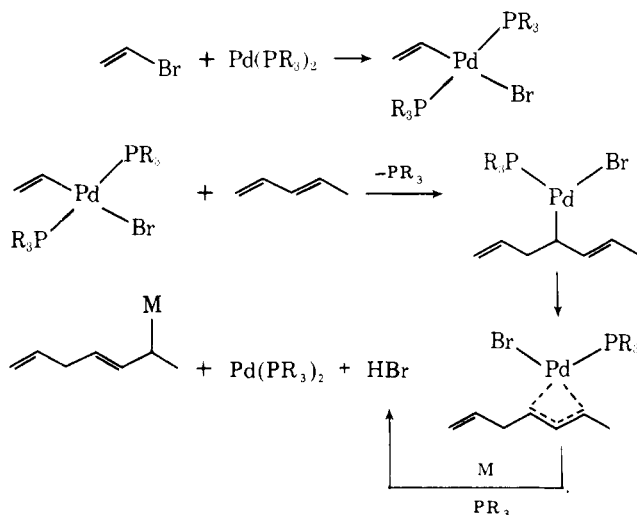
Tertiary 2,5-dienylamines are produced in moderate to good yields when vinylic halides are reacted with conjugated dienes and morpholine or piperidine in the presence of palladium catalysts. The vinylic group always adds to the terminal position of the least-substituted double bond of the diene system. The amine products are easily converted into allylic chlorides by reaction with chloroformate esters.

Palladium-catalyzed arylations of olefins with aryl halides are well known.<sup>1</sup> Similar reactions with vinylic halides have not been as thoroughly investigated. Preliminary results,<sup>2,3</sup> however, suggest that these reactions are also general and have considerable potential in the area of organic syntheses. We have continued the exploration of these reactions and have recently observed facile arylations of conjugated dienes with aryl halides.<sup>4</sup> We now report the logical extension of the reaction to the vinylation of conjugated dienes.

### Results and Discussion

A variety of vinylic halides have been reacted with several conjugated dienes and a secondary amine (morpholine or piperidine) with a palladium catalyst. The reactions carried out and the results obtained are summarized in Table I.

Vinyl bromide, (*E*)-1,3-pentadiene, and morpholine reacted with 1 mol % palladium acetate–2 mol % tri-*o*-tolylphosphine as catalyst in 17 h at 100 °C to form 6-morpholino-1,4-heptadiene in 18% yield. (All yields except where noted are of purified, isolated products.) In this instance, a 3:1 ratio of diene/vinylic halide was used since better yields were obtained than with the usual 1.25:1 ratio. The remainder of the product was polymer and higher boiling materials which were not identified.



The formation of the product in the above reaction can be readily explained on the basis of an addition of the vinylpalladium intermediate to the terminal double bond of the diene followed by cyclization to the  $\pi$ -allylic complex and a final attack of the amine upon the complex with displacement of the palladium–phosphine–halide group. The palladium then undergoes loss of halide ion and oxidatively adds more vinyl bromide to start the cycle again.

In contrast to the formation of the  $\pi$ -allylic complex by a palladium hydride elimination–reverse readdition in the vinylic halide–olefin reaction,<sup>3</sup> in the conjugated diene reaction the  $\pi$ -allylic complex is formed directly from the initial ad-

duct. It is also notable that the attack of the amine upon the  $\pi$ -allylic complex is very selective in that the product appears to be entirely the 6-morpholino adduct and little if any of the possible 4-adduct seems to be formed.

In a much slower reaction, (*Z*)-1-bromopropene, isoprene, and morpholine gave 2-methyl-1-morpholino-2,5-heptadiene in 40% yield along with higher boiling unknown products and polymers. The major point of interest in this example was to determine whether or not the stereochemistry of the (*Z*)-1-bromopropene was retained in the product. The product appeared homogeneous by GLC and NMR; however, IR showed bands characteristic of both *cis* and *trans* olefinic groups. Therefore, the product may be a mixture of isomers. Aside from the stereochemistry about the double bonds, the structure can be assigned from the NMR spectrum. The addition of the 1-propenyl group, therefore, was completely regioselective, adding to the terminal carbon of the less-substituted double bond of the isoprene. This contrasts with the mixture of positional isomers obtained when this halide was added to 1-hexene.<sup>3</sup>

2-Bromopropene reacted as expected from the above results with 1,3-butadiene, isoprene, and (*E*)-1,3-pentadiene, giving amine adducts as the sole or predominant products in 40–60% yields. When piperidine was used as the amine, no triarylphosphine was required.<sup>3</sup>

The reaction of 2-bromopropene with 4-methyl-1,3-pentadiene was more complex. The intermediate  $\pi$ -allylic complex expected from this reaction, I, would have a *gem*-dimethyl group on one of the  $\pi$ -allylic carbons. Few complexes with this structure are known. The 1,1-dimethyl- $\pi$ -allylpalladium chloride phosphine derivatives are known.<sup>5</sup> Structural studies indicated that the carbon bearing the *gem*-dimethyl

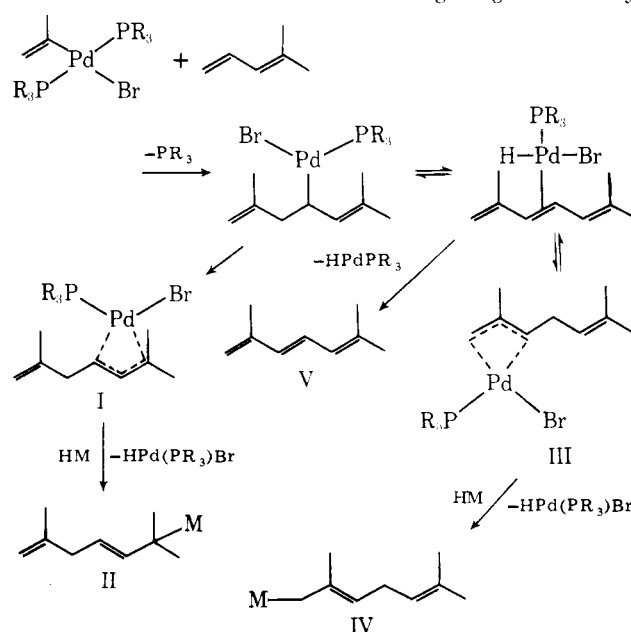


Table I. Vinylation Reactions of Conjugated Dienes at 100 °C<sup>a</sup>

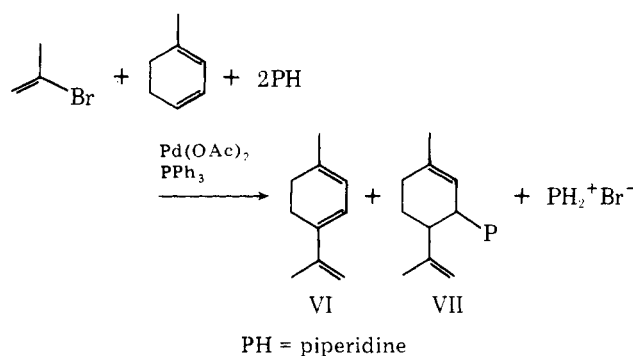
vinyl halide	diene	amine <sup>b</sup>	phosphine	time, h	products, % yield	registry no.
vinyl bromide <sup>c</sup>	( <i>E</i> )-1,3-pentadiene <sup>c</sup>	HM	P( <i>o</i> -tol) <sub>3</sub>	17	6-morpholino-1,4-heptadiene, 18	68965-28-6
( <i>Z</i> )-1-bromopropene	isoprene	HM	P( <i>o</i> -tol) <sub>3</sub>	5 days	2-methyl-1-morpholino-2,5-heptadiene, 40	68965-29-7
2-bromopropene	1,3-butadiene	HP		30	2-methyl-6-piperidino-1,4-hexadiene, 60	68965-30-0
2-bromopropene	isoprene	HM	P( <i>o</i> -tol) <sub>3</sub>	45	2,5-dimethyl-1-morpholino-2,5-hexadiene, 40	68965-31-1
2-bromopropene	( <i>E</i> )-1,3-pentadiene	HM	P( <i>o</i> -tol) <sub>3</sub>	30	2-methyl-6-morpholino-1,4-heptadiene, 55	68965-32-2
2-bromopropene	4-methyl-1,3-pentadiene	HM	P( <i>o</i> -tol) <sub>3</sub> <sup>d</sup>	22	2,6-dimethyl-1,3,5-heptatriene, 12	928-67-6
					2,6-dimethyl-1-morpholino-2,5-heptadiene, 3	68965-33-3
					2,6-dimethyl-6-morpholino-1,4-heptadiene, 26	68965-34-4
2-bromopropene	1,3-cyclohexadiene	HP		24	1-isopropenyl-1,3-cyclohexadiene, 21	68965-35-5
					3-piperidino-6-isopropenylcyclohexene, 35	68965-36-6
					3-piperidino-4-isopropenylcyclohexene, 15	68965-37-7
2-bromopropene	1-methyl-1,3-cyclohexadiene	HP		20	1-isopropenyl-4-methyl-1,3-cyclohexadiene, 39	18368-95-1
					unknown triene, 13	
					4-isopropenyl-1-methyl-3-piperidinocyclohexene, 9	68965-38-8
2-bromopropene	1-methyl-1,3-cyclohexadiene	HP	P( <i>o</i> -tol) <sub>3</sub>	60	1-isopropenyl-4-methyl-1,3-cyclohexadiene, 22	
					unknown triene, 29	
					4-isopropenyl-1-methyl-3-morpholinocyclohexene, 7	68965-39-9
( <i>Z</i> )-3-iodo-3-hexene	( <i>E</i> )-1,3-pentadiene	HM	P( <i>o</i> -tol) <sub>3</sub>	13	undecatrienes, <sup>e</sup> 9	51215-74-5
					4-ethyl-8-morpholino-3,6-nonadiene, 63	68965-40-2
					morpholinoheptadecatrienes, 28	68965-26-4
1-bromo-2-methyl-1-propene	isoprene	HM	P( <i>o</i> -tol) <sub>3</sub>	4 days	2,6-dimethyl-1,3,5-heptatriene, 12	
					2,6-dimethyl-1-morpholino-2,5-heptadiene, 54	
					2,6-dimethyl-3-morpholino-1,5-heptadiene, 8	68965-41-3

<sup>a</sup> Reactants: 10 mmol of vinyl halide, 12.5 mmol of diene, 30 mmol of amine, 1 mol % of palladium acetate, and 2 mol % of phosphine based on the halide (or a 5 or 10 time multiple of these amounts was used). <sup>b</sup> HM = morpholine, HP = piperidine. <sup>c</sup> Reactants: 20 mmol of vinyl bromide, 60 mmol of (*E*)-pentadiene, 50 mmol of morpholine, 1% palladium acetate, and 2% tri-*o*-tolylphosphine. <sup>d</sup> 6% Tri-*o*-tolylphosphine was used. <sup>e</sup> Structures were not established other than by molecular weights (HRMS).

group is trans to the phosphine and less strongly bonded to the palladium than the primary allylic carbon. It is perhaps not surprising, therefore, to find products from the 4-methyl-1,3-pentadiene reaction arising from both the  $\pi$ -complex expected to be formed directly, I, and the one produced by a palladium hydride elimination and reverse readdition, III. The product from the direct complex, II, was obtained in 26% yield (GLC) and the product from the rearranged complex, IV, in 3% yield. There was also produced 12% of conjugated triene, V.

2-Bromopropene was also reacted with two cyclic olefins, 1,3-cyclohexadiene and 1-methyl-1,3-cyclohexadiene. The first diene gave 21% conjugated triene and a 2:1 mixture of the two piperidine adducts (35 and 15%) resulting from attack at both ends of the presumed  $\pi$ -allylic intermediate. Very probably the amine attacks trans to the side of the ring with the propenyl group and there is not a large difference in the environments around the two terminal allylic carbons in this compound.

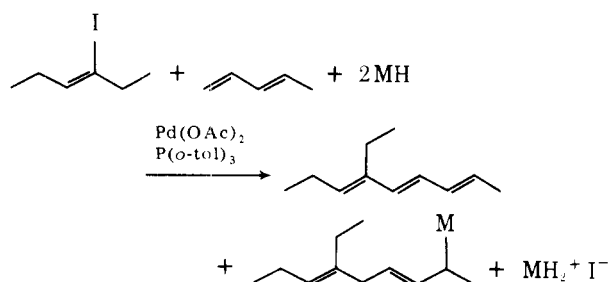
The reaction of 1-methyl-1,3-cyclohexadiene and 2-bromopropene with piperidine gave the expected triene (VI, 39%), another isomer triene (13%), and 4-isopropenyl-1-methyl-3-piperidinocyclohexene (VII, 9%). The last adduct is not the *N*-tertiary alkylpiperidine derivative that might have been expected on the basis of the results obtained with the 4-



methyl-1,3-pentadiene, but rather the compound from attack of the amine at the secondary  $\pi$ -allylic carbon. The difference is apparently due to the more bulky tertiary group in the cyclic compound. The *N*-*tert*-butylpiperidine structure is hindered, and the situation apparently becomes significantly worse if the group is larger than *tert*-butyl. Morpholine reacted similarly to piperidine in this reaction.

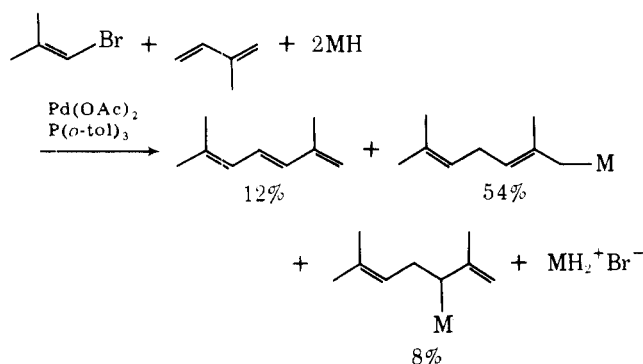
A reaction between (*Z*)-3-iodo-3-hexene,<sup>6</sup> morpholine, and (*E*)-1,3-pentadiene gave 9% trienes and 63% of the expected adduct, 4-ethyl-8-morpholino-3,6-nonadiene.

Qualitatively (*Z*)-3-bromo-3-hexene and (*E*)-1,3-pentadiene gave the same products in approximately the same ratios

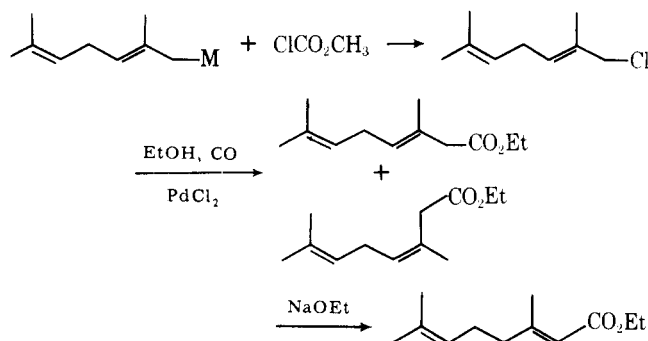


as the iodo compound, but at a slower rate (30 h required).

Finally, 1-bromo-2-methyl-1-propene was reacted with morpholine and isoprene. This bromide added significantly in both directions to 1-hexene,<sup>3</sup> but only terminal addition of the alkyl group was obtained in the reaction with isoprene, although two allylic amine adducts were seen in a ratio of 54% terminal to 8% internal.



The morpholine adducts in this example can be converted into monoterpenes by adding one carbon atom. This was accomplished by first reacting the mixture with methyl chloroformate to give the chloride in 77% yield and then carbonylating the chloride with carbon monoxide and ethanol with a palladium chloride catalyst. The last reaction gave only a 40% yield of an *E* and *Z* mixture of ethyl 3,7-dimethyl-3,6-



octadienoate. Treatment of this diene mixture with sodium ethoxide slowly isomerized it to ethyl geranate.

### Conclusions

The palladium-catalyzed reaction of vinylic halides with conjugated dienes and a secondary amine which produces tertiary 2,5-dienylamines is quite general. Yields are moderate to good considering the specificity and complexity of the reaction. The reaction is of considerable synthetic value since the tertiary amine group can be readily removed by known methods.

### Experimental Section

**Reagents.** The amines, palladium acetate, phosphines, and vinylic halides employed were the same as those used previously.<sup>3</sup> 1,3-Butadiene (Matheson Gas Products), isoprene (Aldrich Chemical Co.), (*E*)-1,3-pentadiene (Chemical Procurement Laboratories), 4-

methyl-1,3-pentadiene (Chemical Samples Co.), and 1,3-cyclohexadiene (Aldrich Chemical Co.) were all used as received from commercial sources. 1-Methyl-1,3-cyclohexadiene was prepared by a published procedure.<sup>7</sup>

**General Procedure for the Reaction of Vinylic Halides with Conjugated Dienes and Amines.** The reactions of all dienes, except butadiene, were carried out in capped heavy-walled Pyrex tubes. A homogeneous solution of 10 mmol of vinylic halide (tube was cooled when vinyl bromide was used), 12.5 mmol of diene, 30 mmol of amine, 1 mol % of palladium acetate based upon the halide, and 2 mol % of the triarylphosphine was prepared in the tube. The air was briefly flushed out with nitrogen, and the tube was capped. The bottle was then heated in a steam bath until GLC analysis of a sample showed that the vinylic halide had all reacted. The products were isolated by diluting the cooled, solid reaction mixtures with aqueous sodium hydroxide, extracting, drying the extracts, and distilling under reduced pressure. For more accurate results, reactions were usually scaled up by a factor of 5 or 10 and carried out in 200-mL Pyrex bottles. In cases where isomers were present, they were usually separated for identification by preparative GLC. Alternatively, yields could be determined by adding an internal standard to the reaction mixtures, diluting with acetonitrile, and analyzing by GLC using sensitivity coefficients determined from isolated samples. Reactions with 1,3-butadiene were carried out in a 60-mL stainless steel bomb because of the pressure involved. Products were isolated as above. When piperidine was the amine, no triarylphosphine was added to the reaction mixtures.

The molecular weights and NMR spectra of the compounds prepared are given in Table II (see note at end of the paper regarding supplementary material).

One example of the reaction is given in detail below.

**2-Methyl-6-morpholino-1,4-heptadiene.** In a 200-mL Pyrex bottle was placed 6.05 g (50 mmol) of 2-bromopropene, 4.25 g (62.5 mmol) of (*E*)-1,3-pentadiene, 13.1 mL (150 mmol) of morpholine, 0.112 g (0.50 mmol) of palladium acetate, and 0.30 g (1.00 mmol) of tri-*o*-tolylphosphine. The bottle was flushed with nitrogen and capped with a self-sealing rubber-lined cap. The homogeneous solution was then heated in a steam bath for 30 h, at which time GLC analyses indicated that the halide had completely reacted. The cooled, solid reaction mixture was then stirred with excess aqueous sodium hydroxide and ether. The ether layer was separated, dried over magnesium sulfate, and distilled under reduced pressure. There was obtained 5.68 g of product, bp 63–76 °C (0.5 mm), which was 89% 2-methyl-6-morpholino-1,4-heptadiene by GLC (55%). The product contained about 4% of (probably) 2-methyl-4-morpholino-1,5-heptadiene and 3% of a morpholine adduct of the pentadiene. A pure sample was isolated by preparative GLC.

**1-Chloro-2,6-dimethyl-2,5-heptadiene.** A solution of 5.0 g (24 mmol) of 2,6-dimethyl-1-morpholino-2,5-heptadiene and 2.8 mL (36 mmol) of methyl chloroformate was magnetically stirred at room temperature for 19 h. The entire solution was then put onto 50 g of silica gel in a chromatographic column, and the chloride was eluted with cyclohexane. Evaporation of the cyclohexane under reduced pressure at room temperature gave 2.95 g (77%) of the chloride:  $M_r$  (by HRMS) found 158.085, calcd 158.086; NMR  $\delta$  1.70 (t, 9 H), 2.70 (t,  $J$  = 6 Hz, 2 H), 3.90 (s, 2 H), 5.00 (t,  $J$  = 6 Hz, 1 H), 5.40 (t,  $J$  = 6 Hz, 1 H).

**Carboethoxylation of 1-Chloro-2,6-dimethyl-2,5-heptadiene.** In the reaction flask of a gasometric apparatus<sup>8</sup> was placed a mixture of 1.59 g (10 mmol) of the chloride, 11 mL of ethanol, and 0.089 g (0.5 mmol) of palladium chloride. The apparatus was sealed and flushed with carbon monoxide at 46 °C. Then 3.8 mL (22 mmol) of diisopropylethylamine was added by syringe through the rubber stopper on the side arm and gas absorption began. The reaction stopped in 3 h after 118 mL of gas had been absorbed. The ethanol was then removed under reduced pressure, and the residue was extracted with ether. The extract was concentrated, and the two major products were separated by preparative GLC. The two expected esters, (*E*)- and (*Z*)-ethyl 3,7-dimethyl-3,6-octadienoate, were in a ratio of about 1:2, respectively. A small amount of ethyl geranate was also seen. This peak increased in size when the mixture was heated at 50 °C with 0.1 M sodium ethoxide in ethanol.

NMR (*E* isomer)  $\delta$  1.25 (t,  $J$  = 7 Hz, 3 H), 1.75 (m, 9 H), 2.75 (t,  $J$  = 7 Hz), 3.10 (s, 2 H), 4.20 (q,  $J$  = 7 Hz, 2 H), 5.3 (m, 2 H);  $M_r$  (HRMS) found 196.148, calcd 196.146.

NMR (*Z* isomer)  $\delta$  1.25 (t,  $J$  = 7 Hz, 3 H), 1.70 (m, 9 H), 2.70 (t,  $J$  = 7 Hz, 2 H), 2.95 (s, 2 H), 4.20 (q,  $J$  = Hz, 2 H), 5.20 (m, 2 H).

**Acknowledgment.** This research was supported by a grant from the National Science Foundation. Some of the palladium

used in the catalyst preparation was loaned to us by the Matthey-Bishop Co., Inc.

**Registry No.**—Vinyl bromide, 593-60-2; (*Z*)-1-bromopropene, 590-13-6; 2-bromopropene, 557-93-7; (*Z*)-3-iodo-3-hexene, 16403-13-7; 1-bromo-2-methyl-1-propene, 3017-69-4; (*E*)-1,3-pentadiene, 2004-70-8; isoprene, 78-79-5; 1,3-butadiene, 106-99-0; 4-methyl-1,3-pentadiene, 926-56-7; 1,3-cyclohexadiene, 592-57-4; 1-methyl-1,3-cyclohexadiene, 1489-56-1; morpholine, 110-91-8; piperidine, 110-89-4; P(*o*-tol)<sub>3</sub>, 6163-58-2; palladium acetate, 3375-31-3; 1-chloro-2,6-dimethyl-2,5-heptadiene, 68965-42-4; (*E*)-ethyl 3,7-dimethyl-3,6-octadienoate, 68965-43-5; (*Z*)-ethyl 3,7-dimethyl-3,6-octadienoate, 16750-89-3.

**Supplementary Material Available:** Table II, containing NMR

spectra, boiling points, and molecular weights of the products prepared (2 pages). Ordering information is given on any current masthead page.

## References and Notes

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## Oxidation of Alcohols by Molybdenum and Tungsten Peroxo Complexes

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*Received July 13, 1978*

It has been demonstrated that peroxo complexes of molybdenum and tungsten oxidize secondary alcohols to ketones. The best yields have been obtained with hydrogen oxidiperoxo(pyridine-2-carboxylato)molybdate(VI) and its tungsten analogue. The latter complex proved to be a good catalyst for oxidation of secondary alcohols to ketones by hydrogen peroxide. The kinetics of the catalytic oxidation are reported, and a mechanism of the reaction is suggested.

Peroxo complexes of molybdenum and tungsten, although known for some time, have not been extensively studied as oxidants for organic substrates. So far peroxo complexes of molybdenum have been used only for stoichiometric epoxidation of olefins<sup>1</sup> and oxidation of cyclohexanone enolate to 2-hydroxycyclohexanone.<sup>2</sup> Our effort has been directed toward the extension of the chemistry of peroxo complexes to other organic substrates. We have shown that, in methanol and in the presence of catalytic quantities of molybdenum and tungsten peroxo complexes stabilized by pyridinecarboxylato ligands, 2-methylcyclohexanone is oxidized to a mixture of methyl 6-hydroxyheptanoate and methyl 6-oxoheptanoate.<sup>3</sup> This finding suggested to us that methyl 6-oxoheptanoate may be a product of oxidation of methyl 6-hydroxyheptanoate. Therefore, a study of secondary alcohol oxidation by group 6 metal peroxo complexes has been initiated. We now wish to report the use of molybdenum and tungsten peroxo complexes as stoichiometric oxidants of secondary alcohols as well as catalysts for oxidation of secondary alcohols by H<sub>2</sub>O<sub>2</sub>.

### Results and Discussion

**Peroxo Complexes as Stoichiometric Oxidants.** Four alcohols were selected as representatives of different classes of secondary alcohols. For the purpose of comparison, the reaction conditions were chosen to be analogous to those used for oxidation of cyclic ketones<sup>3</sup> without any attempt for optimization.

The results of secondary alcohol oxidation by different peroxo complexes of molybdenum and tungsten are summarized in Table I. The complexes containing monodentate ligands such as hexamethylphosphoric triamide (HMPA) as in M(O)(O<sub>2</sub>)<sub>2</sub>(HMPA)(H<sub>2</sub>O) (1, M = Mo; 2, M = W)<sup>4</sup> or nicotinic acid as in W(O)(O<sub>2</sub>)(C<sub>5</sub>H<sub>4</sub>NCO<sub>2</sub>H)(H<sub>2</sub>O)<sup>5</sup> (3) decompose to "blue metal oxides" in the course of oxidation. Therefore, no ketone or low yields of ketones are obtained. Introduction of a tridentate pyridine-2,6-dicarboxylato ligand as in M(O)(O<sub>2</sub>)[C<sub>5</sub>H<sub>3</sub>N(CO<sub>2</sub>)<sub>2</sub>](H<sub>2</sub>O)<sup>6</sup> (4, M = Mo; 5, M = W)

renders the complex completely inactive. Only complexes stabilized by the bidentate picolinato ligand such as in H<sup>+</sup>[M(O)(O<sub>2</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>NCO<sub>2</sub>)<sub>2</sub>]-H<sub>2</sub>O (6, M = Mo; 7, M = W)<sup>6</sup> oxidize secondary alcohols to ketones in good yields. A 1-mol amount of complex 6 or 7 oxidizes more than 1 mol of secondary alcohol, yielding up to 1.7 mol of ketone per mol of the peroxo complex (Table I). This result suggests that both peroxo moieties in the complexes 6 and 7 are active, although the second one may react more slowly than the first one. Even though the reaction mixtures were analyzed only at the time indicated in Table I, the molybdenum complex 6 seems to react much more slowly than the corresponding tungsten complex 7. During the oxidations a precipitate is formed. In the case of 7 the precipitate was isolated and shown, by IR and iodometric titration, to contain only metal oxo bonds and no peroxo bonds. Elemental analysis of the isolated precipitate indicated the presence of about 1 mol of picolinic acid per mol of WO<sub>3</sub>·H<sub>2</sub>O, suggesting a tungsten oxo complex W(O)-<sub>3</sub>(C<sub>5</sub>H<sub>4</sub>NCO<sub>2</sub>H)(H<sub>2</sub>O).

**Peroxo Complex 7 as Catalyst.** Regeneration of peroxo complexes by the reaction of oxo complexes with hydrogen peroxide is very fast.<sup>5</sup> Therefore, it became apparent that secondary alcohols should be oxidized by hydrogen peroxide in the presence of catalytic quantities of peroxo complexes 6 or 7. The data summarized in Table II indeed demonstrate that the complex 7 is an active catalyst. The molybdenum analogue 6, which is a slow oxidant of secondary alcohols (Table I), was found to be very inefficient. The catalytic oxidation is not limited to secondary alcohols. Primary alcohols can be oxidized as well, though at a lower rate.<sup>7</sup>

**Kinetics of the Catalytic Oxidation.** In order to gain a better understanding of the reaction mechanism, the oxidation of cyclohexanol was followed by iodometric titration. At the end of every run the amount of cyclohexanone formed was analyzed<sup>8</sup> by GC and shown to correspond to the amount of consumed hydrogen peroxide. Therefore, oxidation of methanol is negligible and it does not contribute to the consumption of hydrogen peroxide. In the kinetic runs the ratio of cy-