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Oxidation of Benzylic Derivatives with Dioxygen Catalyzed by Mixed Addenda Metallophosphate Containing Vanadium and Molybdenum

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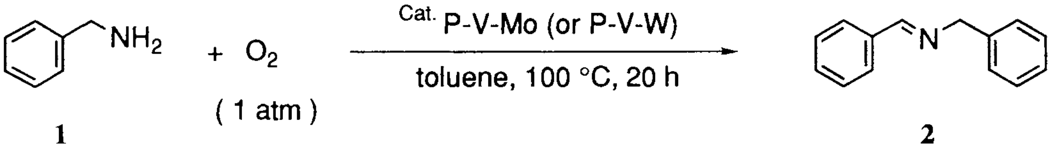
Mixed addenda heteropolyoxometalate, NPV_6Mo_6, was found to be an efficient catalyst for the oxidative dehydrogenation of a variety of benzylic amines to the corresponding Schiff-base imines with molecular oxygen in toluene solution. Under the same reaction conditions, isochroman and indan were respectively oxidized to 3,4-dihydroisocoumarin and 1-indanone with high selectivity.

Heteropolyoxometalates have been attracted interest as catalysts for oxidations of a wide variety of organic compounds with hydrogen peroxide[1)] and molecular oxygen (dioxygen).[2)] In particular, mixed addenda heteropolyoxometalates such as $H_5PV_2Mo_{10}O_{40}$ catalyze the oxidation of various substrates with dioxygen as primary oxidant in both photochemical[2a,b)] and thermal systems, e.g., oxybromination[2c)] and oxidation of sulfides,[2d)] oxidative cleavage of ketones,[2e)] oxidative dehydrogenation of dienes,[2f)] alcohols, and amines.[2g)] Therefore, our attention has been focused on the direct oxidation of organic substrates with dioxygen by mixed addenda 12-metallophosphates, P-V-Mo and P-V-W systems.

In this letter, we would like to report a highly selective oxidation of benzylic derivatives with dioxygen catalyzed by mixed addenda metallophosphates. The oxidation of benzylamine (**1**) to the corresponding Schiff-base imine (**2**) with dioxygen was chosen as a model reaction and carried out by using the following V-based metallophosphates as catalysts; i.e., $(NH_4)_5H_4PV_6W_6O_{40}\cdot 6H_2O$ (**3**),[3)] $(NH_4)_3HPVMo_{11}O_{40}\cdot 7.5H_2O$ (**4**),[4)] $H_5PV_2Mo_{10}O_{40}\cdot 32H_2O$ (**5**),[4)] $H_4PVMo_{11}O_{40}\cdot 34H_2O$ (**6**),[4)] and NPV_6Mo_6 (**7**).[5)]



1 **2**

A typical reaction is as follows: **7** (35 mg, 16 wt%) was added to a solution of **1** (2 mmol) in toluene (4 ml). The flask was flashed with oxygen and equipped a baloon filled with about 5 L of O_2. The mixture was allowed to react under stirring at 100 °C for 20 h. The yield of product was determined by GLC.

Table 1 shows the results for the oxidation of **1** with dioxygen by various mixed-addenda heteropolyoxometalates, $PV_nM_{12-n}O_{40}^{(3+n)-}$, **3-7**, and $PM_{12}O_{40}^{3-}$, **8** and **9** (M = W or Mo). All metallophosphates involving vanadium catalyzed the conversion of **1** to **2** in fair to good yields, but simple metallophosphates such as $H_3PW_{12}O_{40}{\cdot}nH_2O$ (**8**) and $H_3PMo_{12}O_{40}{\cdot}nH_2O$ (**9**) were inert in the present reaction. Among the vanadium metallophosphates examined, **7** was found to be the best catalyst. The catalytic activity of the **5**, which shows high activity in the oxidative cleavage of ketones[2e)] and the oxidative dehydroganation of diene,[2f)] was modarate in the present reaction.

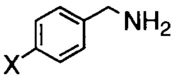
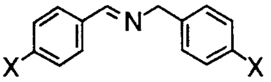
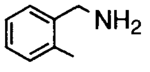
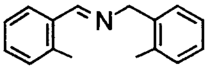
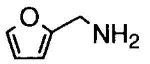
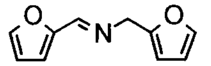
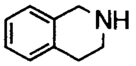
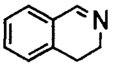
Table 1. Oxidation of Benzylamine (**1**) to Schiff-base Imine (**2**) with Dioxygen by Various V-based Metallophosphates[a)]

Run	Catalyst	Solvent	Temp /°C	Conv. / %	Yield / %[b)]
1	$(NH_4)_5H_4PV_6W_6O_{40}{\cdot}6H_2O$ (**3**)	toluene	100	62	74
2	$(NH_4)_3HPVMo_{11}O_{40}{\cdot}7.5H_2O$ (**4**)	toluene	100	67	54
3	$H_5PV_2Mo_{10}O_{40}{\cdot}32H_2O$ (**5**)	toluene	100	44	89
4	$H_4PVMo_{11}O_{40}{\cdot}34H_2O$ (**6**)	toluene	100	60	97
5[c)]	NPV_6Mo_6 (**7**)	toluene	100	81	>99
6[c)]	**7**	acetonitrile	rf.	45	42
7[c)]	**7**	1,2-dichloroethane	rf.	92	34
8	$H_3PW_{12}O_{40}{\cdot}nH_2O$ (**8**)	toluene	100	<1	trace
9	$H_3PMo_{12}O_{40}{\cdot}nH_2O$ (**9**)	toluene	100	14	86

a) Reaction conditions : **1** (2 mmol), toluene (4 ml), catalyst (1 mol%), 20 h, O_2 1 atm.b) GC yields based on the **1** consumed. c) **7** (35 mg, 16 wt% to **1**) was used.

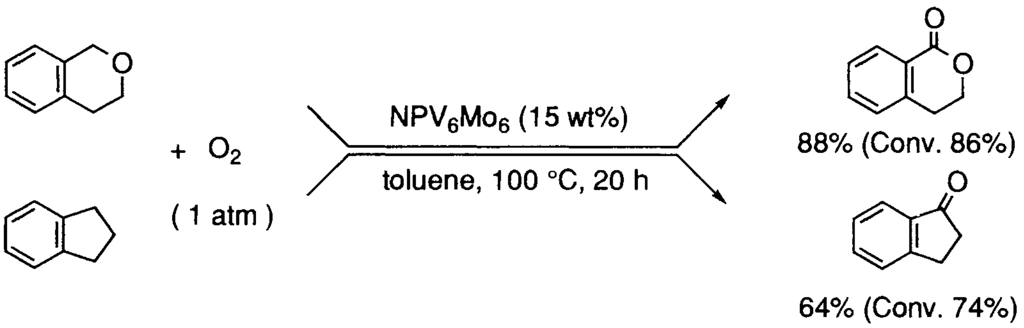
On the basis of these results, various amines were oxidized in the presence of a catalytic amount of **7** in toluene under oxygen atmosphere (Table 2). p-Chlorobenzylamine was converted into the corresponding Schiff-base imine in low yield. However, p-methyl- and p-methoxybenzylamines bearing an electon donating group on the aromatic ring gave imines in fair to good yields. Furfurylamine was also oxidized to imine in 52% yield. Aliphatic primary amines such as octylamine were difficult to oxidize with high selectivity because of occurence of the over-oxidation. In the case of 1,2,3,4-tetrahydroisoquinoline, the dehydrogenation proceeded selectively to give 3,4-dihydroisoquinoline in good yield. It is probable that benzylic amines are converted into the corresponding Schiff-base imines via a similar way as that of the oxidation of **1** to **2** by $Na_5PV_2Mo_{10}O_{40}$ on charcoal.[2g]

Table 2. Oxidative Dehydrogenation of Various Amines with Dioxygen Catalyzed by **7**[a]

Run	Substrate	Product	Conv. / %	Yield / %[b]
				
1	X = H		81	>99
2	Cl		46	71
3	CH_3		52	79
4	CH_3O		85	96
5			17	96
6			-	52[c]
7[d]	$n\text{-}C_8H_{17}NH_2$	$n\text{-}C_7H_{15}CH{=}NC_8H_{17}\text{-}n$	>99	22
8			82	>99

[a] Reaction conditions: amines (2 mmol), toluene (4 mmol), **7** (35 mg), 100 °C, 20 h, O_2 1 atm. [b] GC yields based on substrates consumed. [c] Determined by NMR. [d] Toluene (6 ml) was used.

Hoping to the further utilization of this system, we have extended to the oxidation of isochroman and indan under these reaction conditions. It was found that benzylic carbons of these compounds were selectively oxidized to give 3,4-dihydroisocoumarin and 1-indanone in relatively good yields. It is noteworthy that the direct C-H bond activation can be achieved by molecular oxygen and the NPV_6Mo_6 under relatively mild conditions.



Further work is under way to apply this system to other substrates and to explore a new catalyst having higher activity for these reactions.

Reference

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5) NPV$_6$Mo$_6$ (**7**) was prepared by modifing the method described for the preparation of $(NH_4)_5H_4PV_6W_6O_{40}\cdot 6H_2O$ (**3**)[3] using $Na_2MoO_4\cdot 2H_2O$ in place of $Na_2WO_4\cdot 2H_2O$: To a solution of $NaVO_3$ (7.32 g, 60 mmol) in water (38 ml) was added $Na_2MoO_4\cdot 2H_2O$ (8.22 g, 34 mmol) in water (12 ml). To the resulting solution was added dropwise 85% H_3PO_4 (4.2 g, 35 mmol) in water (10 ml), and the mixture was stirred for 1 h at 95 °C. After cooling to room temperature, the solution was added to a saturated ammonium chloride solution (150 ml) to give a brown precipitate (ca. 8 g). The resulting precipitate was recrystallized two times from water to form clean orange crystal of **7**. ^{31}P NMR of the **7** gave a spectrum consisting of a number of signals. This shows that the **7** is a mixture having different compositions of V and Mo. However, **7** is reproducible material, as indicated by the almost same combustion analyses as follows: H, 2.94 ± 0.04; N, 4.55 ± 0.05. IR (KBr): 3570, 3125, 1637, 1400, 984, 954, 840, 742 cm^{-1}.

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