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SELECTIVE ALLYLIC REARRANGEMENT WITH TUNGSTEN CATALYST

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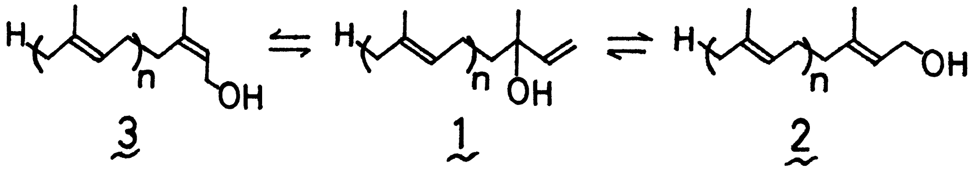
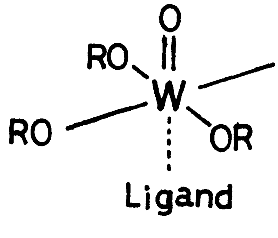
Selective thermal rearrangement of allylic alcohols proceeds in the presence of various $O{=}W(OR)_4$·Ligand catalysts which are more stable than $O{=}W(OR)_4$ catalyst and are several times more active than $O{=}V(OR)_3$ catalyst.

Catalytic rearrangement of allylic alcohols has proved a valuable synthetic tool particularly for industrial production of terpene alcohols (2, 3) and extensive study has been devoted to oxo-metallic catalyst of $O{=}V(OR)_3$.1,2) On the other hand, only a few example has been reported of the rearrangement with tungsten catalyst. Chabardes et al1) reported that the rearrangement of linalool 1a (n=1) to geraniol 2a and nerol 3a proceeded with $O{=}W[OSi(C_6H_5)_3]_4$ catalyst in 74% selectivity3). However, according to our experiment the catalyst is quite unstable under the reaction conditions [0.01 mol% v.s. 1a; 200°C], and the selectivity which shows ca. 90% at the beginning of the reaction always decreases drastically by accompanying the dehydration with progress of the reaction near to equilibrium. Here we wish to describe more stable $O{=}W(OR)_4$ Ligand catalysts 4 which are several times more active than the known $O{=}V(OR)_3$ catalyst with high selectivity even in the equilibrium state.





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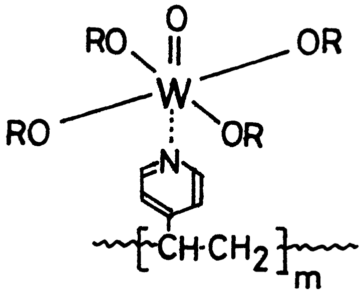

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Catalysts were prepared by the following procedure: Dry methanol (30 ml) was added to a mixture of $O{=}WCl_4$ (11.05 g) in dry benzene (100 ml) to reflux for 1 hr under nitrogen atmosphere. Then ammonia gas was introduced at room temperature for 3 hr, and excess methanol was distilled off from the system to obtain $O{=}W(OCH_3)_4$.4) A mixture of triethylsilanol (13 g) and pyridine (6 ml) was added and the reaction temperature was elevated until no more methanol could be distilled off (ca. 80°C). After cooling the precipitated NH_4Cl was filtered off and the filtrate was evaporated to obtain $O{=}W[OSi(C_2H_5)_3]_4 \cdot$pyridine as white needles (22.2 g; yield 85%).5) The pyridine ligand could not be expelled even if the catalyst is heated at 100°C under reduced pressure.

Allylic rearrangement was carried out by heating **1** with 0.01 mol% of the catalyst at 180-200°C under nitrogen atmosphere. As shown in Table 1 the selectivity of the reaction is held constant at 92-95% even in the equilibrium state [**1**:**2**:**3**=60:25:15; 200°C]. To compare the activity of $O{=}W(OR)_4 \cdot$Ligand with $O{=}V(OR)_3$, the former is several times more active than the latter with similar selectivity [see Table 2; The amount of tungsten catalyst required for the same reaction rate with vanadium catalyst is ca. 1/7]. The superiority of the tungsten catalyst in industrial aspect lies in separation of the catalyst from the reaction mixture by flash distillation: One of the most important process for industrial production of geraniol **2a** is rectification of the mixture of **2a** and **3a** obtained after removal of **1a**. The shortcoming of $O{=}V(OR)_3$ catalyst is that a trace of the catalyst is also distilled off under the conditions of flash distillation to cause reverce isomerization of **2**+**3** → **1** in rectification process. In the case of tungsten catalyst its separation is carried out completely by flash distillation.

Next approach to save energy in separation process is to employ a heterogeneous system by using polymeric catalyst **5** containing a ligand of poly (4-vinylpyridine) cross-linked with 15% of divinylbenzene: The catalyst is thought to be separable from the reaction mixture by filtration. Unfortunately, however, the attempt resulted in failure because the polymeric ligand was partially dissolved(or decomposed)under the reaction conditions, and the loss of the catalyst after filtration was ca. 15%/one batch.

In conclusion the modified new $O{=}W(OR)_4 \cdot$ Ligand catalyst are several times more active than the known $O{=}V(OR)_3$ catalyst with similar selectivity.6) The recycling experiment (4 cycles) showed that the reaction proceeded in 93%

selectivity, and application to the synthesis of all E-farnesol (**2b**; n=2) and all E-geranylgeraniol (**2c**; n=3) was carried out in ca. 94% selectivity.

Table 1. Allylic rearrangement of **1a** with various $O{=}W(OR)_4\cdot$Ligand catalysts. (0.01 mol%; 200°C)

4	R=	Ligand=	Reaction Time (hr)	Conversion of **1a** (%)	Selectivity of **2a**+**3a** (%)
a	CH_3	Pyridine	3	39	94
b	C_2H_5	Pyridine	1	22	94
			3	30	92
c	$Si(C_2H_5)_3$	Pyridine	1	26	96
			2	35	96
			3	39	95
d	$Si(C_2H_5)_3$	Dicyclohexylamine	3	39	92
e	$Si(C_2H_5)_3$	Cyclohexylamine	3	32	92
f	$Si(C_2H_5)_3$	Tricyclohexylphosphine	3	38	94

Table 2. Comparison of the activity of $O{=}W(OR)_4\cdot$ Ligand with $O{=}V(OR)_3$ catalyst.

Catalyst (mol% v.s. **1a**)	$O{=}V(OBu^{tert})_3$ (54×10^{-3})		$O{=}W(O\text{-}Linalyl)_4\cdot$ pyridine (7.4×10^{-3})	
Reaction Temp.	200°C		195-197°C	
Teaction Time (hr)	Conversion of **1a** (%)	Selectivity of **2a**+**3a** (%)	Conversion of **1a** (%)	Selectivity of **2a**+**3a** (%)
1	20	97	28	95
1.5	28	95	34	96
2	36	96	39	95
2.5	38	97	40	95

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References

1) P. Chabardes, K. Kuntz, and J. Varagnat, Tetrahedron, 33, 1775 (1977): Brit. P. 1,204,754.

2) a)H. Pauling, D. A. Andrews, and N. C. Hindley, Helv. Chim. Acta, 59, 1233 (1976).

b)M. B. Erman, I. S. Aul'chenko, L. A. Kheifits, V. G. Dulova, Ju. N. Novikov, and M. E. Vol'pin, Tetrahedron Lett., 1976, 2981.

3) Chabardes et al used the word of "yield of **2a**+**3a**" (=74%) relative to the conversion of **1a** (=30%). In this paper "selectivity of the reaction" which is widely variable with progress of the reaction is used synonymously and is defined as hereunder:

Selectivity=[Yield of (**2** + **3**)/ Conversion of **1**]×100 %

4) H. Funk and W. Baumann, Z. anorg. u. allgem. Chem., 231, 265 (1937); ibid, 304, 238 (1960).

5) The catalyst in solid state is relatively unstable to air and moisture, and the melting point (>100°C) could not be measured. The purity of this catalyst is measured to be 99% by quantitative X-ray fluorescent analysis of the ratio of Si/W (=3.96). IR (KBr) 1450, 1410, 1235, 895, and 740 cm^{-1}. Anal. Found: C; 43.10, H; 8.16, N; 1.62. Calcd. for $C_{29}H_{65}NO_5Si_4W$: C; 43.32, H; 8.15, N; 1.74.

6) There are some differences and similarity between $O{=}W(OR)_4$·Ligand and $O{=}W(OR)_4$ or $O{=}V(OR)_3$ catalyst in other systems.

i) In the case of rearrangement of propargylic alcohol of dehydrolinalool to citral, $O{=}W(OR)_4$·Ligand catalysts were quite inactive, and 2,6,6-trimethyl-2-ethynyltetrahydropyran which was reported to be obtained mainly with tungsten catalyst[2b] could not be detected.

ii) Epoxidation of allylic alcohols with $O{=}W(OR)_4$·Ligand catalyst proceeds similarly with $O{=}V(OR)_3$ catalyst.

Further investigations to these problems are now in progress in our laboratories and some results will be reported in near future.

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