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A MEERWEIN - PONNDORF - VERLEY TYPE REDUCTION OF α,β UNSATURATED KETONES TO ALLYLIC ALCOHOLS CATALYZED BY MgO

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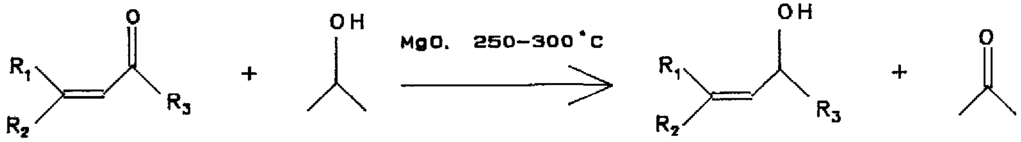
Abstract. Allylic alcohols are obtained with an unprecedented simple method by chemoselective hydrogen transfer reduction of α,β unsaturated ketones catalyzed by MgO.

Selective reduction of α,β unsaturated ketones to the allylic alcohols is a challenging problem since it usually requires an excess of expensive reagents and overreduction *products are often obtained*[1,2].

While reduction of saturated ketones or α,β unsaturated aldehydes by hydrogen transfer from alcohols is catalyzed by a variety of metal oxides[3], α,β unsaturated ketones are quite resistant to reduction and no allylic alcohols are obtained[4].

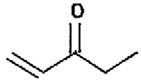
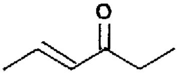
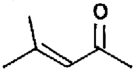
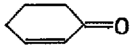
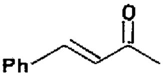
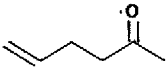
We report the unprecedented observation that α,β unsaturated ketones can be chemoselectively reduced to allylic alcohols in good yields (50-90%) in hydrogen transfer conditions in a flow system with MgO as catalyst[*] and propan-2-ol as hydrogen donor:



The results are reported in the Table. Substantial amount of product with terminal double bond is obtained in run 3 (36% of 4-methyl-4-penten-2-ol). This result is somehow expected since the thermodynamic mixture of monoolefins usually enriches in terminal isomers increasing the temperature[5]. For comparison's sake, the reduction of a non conjugated unsaturated ketone (5-hexen-2-one) is also reported. The use of vapor phase flow system turned out to be an essential requirement. In fact, when the reactions were carried out in batch, a wide range of condensation products was obtained in addition to some saturated ketone. The high basicity of MgO combined with the long reaction times probably promotes such condensation reactions. By contrast, in the flow system short contact times (LHSV= 9.0 h^{-1}) are achieved, hence formation of undesirable byproducts is minimized.

The reduction of α,β unsaturated ketones occurs at the carbonyl group with high chemoselectivity and almost no reduction of the carbon-carbon double bond is observed. In some cases, however, competitive isomerization of the carbon-carbon double bond takes place. The use of MgO as catalyst seems to be crucial; in fact other oxides such as CaO, Al_2O_3, ZnO were tested under various conditions but gave poor selectivities in all cases.

Table. Hydrogen transfer reduction of unsaturated ketones[a].

Run	Enone	Conversion[b] (%)	α,β Unsaturated alcohol (%)	Non conjugated enone (%)	β,γ Unsaturated alcohol (%)	Others (%)
1.		48	43	–	–	5
2.		89	71	1	4	13
3.		91	52	1	36	2
4.		37	15	7	9	6
5.		77[c]	75	–	–	2
6.		95	90[d]	1[e]	4[c]	–

[a] Reaction conditions: MgO (0.005 mol), 250°C, flow of reagents 0.2 ml/min, mol(propan-2-ol) /mol(unsaturated ketone) = 20. [b] Non optimized conditions. The analyses of the reaction mixtures were performed by means of GLC, using n-heptane as internal standard, the composition of the reaction mixture was determined after 1 hour in steady state conditions. [c] On a larger scale (MgO 0.02 mol, flow of reagents 0.8 ml/min), 2.8 g of isolated product can be obtained from 3.1 g of starting reagent. [d] 5-hexen-2-ol. [e] Mixtures of internal isomers.

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References and Notes

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[*] A tubular stainless steel reactor (length 14 cm x 1/4") is employed. The catalyst powder is placed between two layers of granular quartz. The liquid reactants are fed into the reactor with a high pressure liquid pump. At the outlet of the reactor a 50 cm piece of tubing (1/16", 0.020" i.d.) is used as condenser. High surface area MgO (220 m²/g) was synthesized *in situ* by thermal treatment of $Mg(OH)_2$ (350°C) in air flow for 4 hours. With this catalyst at 300°C as many as 7 moles of substrate per mole of MgO can be converted before it deactivates. Catalytic activity is easily restored by air flow through the system at 350°C.

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