

SELECTIVE HYDROGENATION OF  $\alpha$ ,  $\beta$  - UNSATURATED ALDEHYDES TO  
UNSATURATED ALCOHOLS OVER OSMIUM CATALYSTS

Paul N. Rylander and Duane R. Steele  
Engelhard Industries, Newark, N.J. U.S.A.

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Selective catalytic hydrogenation of an  $\alpha$ ,  $\beta$ -unsaturated aldehyde to a saturated aldehyde is achieved easily (1), but selective reduction to afford unsaturated alcohols is a formidable task. Unsaturated alcohols have been prepared in this manner over platinum oxide (2), platinum-on-carbon (3), and platinum-on-calcium carbonate (3), each catalyst being inhibited by at least two additional metals. Ruthenium inhibited by lead has also been used (4). The appropriate modification of these catalysts, necessary to achieve satisfactory results, varies with each catalyst and is obtained only by trial and error.

We wish to report now that reduced osmium supported on alumina or preferably on carbon are excellent catalysts for conversion of unsaturated aldehydes to unsaturated alcohols. Good yields of allyl alcohol, crotyl alcohol and cinnamyl alcohol were obtained by hydrogenation of acrolein, crotonaldehyde, and cinnamaldehyde, respectively, both with and without solvent. For example, 10 gm cinnamaldehyde in 25 ml isopropanol was reduced in a stirred autoclave over 1 gm 5% osmium-on-carbon at 750 - 1000 psig and 100°C to afford cinnamyl alcohol in 95% yield, based on gas chromatographic analysis. The reduction ceased after absorption of one mole of hydrogen. Reduction of crotonaldehyde and acrolein under the same conditions afforded the corresponding unsaturated alcohols in 90% and 73% yields, respectively.

Similar results were obtained over 5% osmium-on-alumina but the rates of reduction were about half. Higher hydrogenation temperatures increased the rate but at the expense of a lower selectivity. The activity of the osmium catalysts increased after reuse, a phenomenon frequently observed with ruthenium catalysts.

These selective reductions are apparently not applicable to  $\alpha$ ,  $\beta$ -unsaturated ketones; hydrogenation of mesityl oxide afforded methyl isobutyl ketone.

#### REFERENCES

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