Ruthenium-catalysed Oxidation of Allyl Alcohols by Molecular Oxygen

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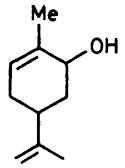
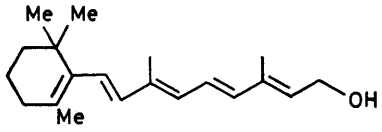
Summary Ruthenium(II) catalyses the homogeneous oxidation of allyl alcohols to carbonyl compounds by molecular oxygen under mild conditions.

RECENT studies have shown that ruthenium complexes catalyse the homogeneous oxidation of alcohols to ketones or aldehydes by organic oxidants such as conjugated ketones[1] and amine *N*-oxides.[2] We describe here a successful ruthenium-catalysed oxidation of allyl alcohols to α,β-unsaturated carbonyl compounds by molecular oxygen under mild conditions.

In a typical procedure, a solution of $RuCl_2(PPh_3)_3$ (0·1 mmol) and (*E*)-2,7-dimethylocta-2,6-dien-1-ol (geraniol) (3 mmol) in 1,2-dichloroethane (25 ml) was stirred at room temperature for 48 h in a flask attached to a gas burette filled with O_2 at 1 atm. The product was isolated by column chromatography (SiO_2) and its structure assigned by i.r., n.m.r., and mass spectral analyses. Results for several allylic alcohols are summarized in the Table.†



(1)



(2)

TABLE. Oxidation of allyl alcohols $R^1CH{=}CHCH(OH)R^2$ to carbonyl compounds $R^1CH{=}CHC(:O)R^2$ by molecular oxygen.

Example	Alcohol	% Yield of product
1	3-Methylbut-2-en-1-ol	46
2	(*E*)-3,7-Dimethylocta-2,6-dien-1-ol	67
3	(*Z*)-3,7-Dimethylocta-2,6-dien-1-ol	92
4	3-(2,6,6-Trimethylcyclohex-1-enyl)prop-2-en-1-ol	100
5	(−)-Carveol (**1**)	92
6	(*E*)-4-Acetoxy-2-methylbut-2-en-1-ol	86
7	(*E*)-2-Methyl-4-phenylthiobut-2-en-1-ol	47
8	Retinol (**2**)	57

Characteristic features of these oxidations are as follows. (i) The reaction proceeds with retention of stereochemistry (compare examples 2 and 3). (ii) Other functional groups such as sulphide are stable under the reaction conditions (example 7). Furthermore, it is worth pointing out that the labile retinol can also be oxidized into retinal by molecular oxygen by this system.‡

The ruthenium complexes $RuBr_2(PPh_3)_3$ and $RuH(OAc)(PPh_3)_3$ could also be used in these oxidations, but hydrated $RuCl_3$, which is known to have catalytic activity in the oxidation of amines and saturated secondary alcohols,[3] did not give satisfactory results.§ The catalytic oxidations could also be performed in other solvents such as benzene, 1,2-dimethoxyethane, ethyl acetate, acetone, and methanol, but solvents of strong co-ordinating ability, *e.g.* acetonitrile, inhibited the oxidations. ^{31}P n.m.r. analysis showed that the triphenylphosphine ligand in the catalysts was oxidised to triphenylphosphine oxide in the early stages of the oxidation (within *ca.* 5 min).

The mechanism of these catalytic oxidations probably involves formation of a ruthenium alkoxide,[4] which undergoes β-elimination to produce the carbonyl compound and a ruthenium hydride (or its equivalent) which could be oxidized by molecular oxygen.

The oxidation of allyl alcohols into unsaturated carbonyl compounds by molecular oxygen under mild conditions by the present system contrasts with palladium(II)-catalysed oxidations where olefinic alcohols poison the catalyst by strong complexation.[5]

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† No attempt has been made to optimize the reaction conditions.

‡ 2,6-Dimethylpyridine (1—1·5 equiv. with respect to the catalyst) was added. Unfavourable results were obtained without addition of base; other amines such as pyridine poisoned the catalyst. A trace of acid (HCl?) derived from the catalyst may decompose the retinol and/or retinal in the absence of added base.

§ Dehydration, isomerization, and other complex reactions predominated over the desired oxidation.

[1] Y. Sasson and J. Blum, *Tetrahedron Lett.*, 1971, **2167**; Y. Sasson and G. L. Rempel, *ibid.*, 1974, **4133**; *Can. J. Chem.*, 1974, **52**, 3825; S. L. Regan and G. M. Whitesides, *J. Org. Chem.*, 1972, **37**, 1832.
[2] K. B. Sharpless, K. Akashi, and K. Oshima, *Tetrahedron Lett.*, 1976, **2503** and references therein.
[3] R. Tang, S. E. Diamond, N. Neary, and F. Mares, *J. Chem. Soc., Chem. Commun.*, 1978, **562**.
[4] Y. Sasson and J. Blum, *J. Chem. Soc., Chem. Commun.*, 1974, **309**.
[5] T. F. Blackburn and J. Schwartz, *J. Chem. Soc., Chem. Commun.*, 1977, **157**.