Fast Generation and Stabilization of 2-Methylprop-1-en-1-ol with $[Rh(CO)(PPh_3)_3]ClO_4$

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2-Methylprop-1-en-1-ol is rapidly generated and stabilized during the isomerization of 2-methylprop-2-en-1-ol to 2-methylpropanal with $[Rh(CO)(PPh_3)_3]ClO_4$.

Enols have been generated by various methods and investigated although they rapidly undergo tautomerization to the corresponding carbonyl compounds.[1—9] Two different approaches have been used for observation of significant amounts of enols: (i) introducing appropriate substituents at the carbon–carbon double bond is effective in stabilizing enols by slowing the tautomerization to the carbonyl compounds;[1—3] (ii) relatively fast generation (compared with the subsequent tautomerization) of simple enols by different synthetic methods has produced sufficiently high concentrations of enols for various studies.[4—7]

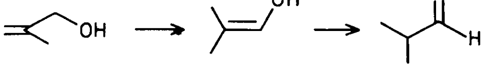
During the investigation of the catalytic reactions of unsaturated alcohols with rhodium(I) complexes, we have now found that a considerable concentration (0.72 M in $CDCl_3$) of an enol, 2-methylprop-1-en-1-ol (**1**), was obtained in the isomerization of 2-methylprop-2-en-1-ol (**2**) to 2-methylpropanal (**3**) with $[Rh(CO)(PPh_3)_3]ClO_4$ (**4**).[10]

Detailed ^1H n.m.r. data have previously been reported for (**1**) {δ 1.47 and 1.52 [2d, $=C(CH_3)_2$], 6.20 (m, =CHOH) in CD_3COCD_3 and D_2O}.[5] The spectra in Figure 1 clearly show the generation and disappearance of (**1**) during the isomerization of (**2**) to (**3**). The OH signal due to (**2**) disappears immediately upon mixing with (**4**) (see Figure 1b).

The isomerization of other unsaturated alcohols (prop-2-en-1-ol, but-3-en-2-ol, but-2-en-1-ol, 3-methylbut-2-en-1-ol) to the corresponding carbonyl compounds with (**4**) is much slower than that of (**2**),[11] and enols have not been detected during the isomerization of other unsaturated alcohols. Accordingly, we suggest that the enol (**1**) can be observed since it is generated fast enough to compete with the subsequent tautomerization to (**3**).

The isomerization [equation (1)] was followed by measuring ^1H n.m.r. spectral changes during the reaction in the δ 4.5—10 region over which a fast scanning for the integration of the signals of (**1**), (**2**), and (**3**) took only 33 seconds. Relative amounts of (**2**), (**1**), and (**3**) were determined by the ratios of the signals at δ 4.91, 6.20, and 9.65, respectively, using the multiplet due to PPh_3 as a standard.

I.r. spectral changes at the later stage of the reaction, after all of (**2**) had disappeared, show ν_{O-H} (*ca.* 3400 cm^{-1}) and ν_{C-OH} (*ca.* 1140 cm^{-1}) bands which rapidly disappear. Decreases in the concentration of (**1**) at the later stage of the reaction where no starting material (**2**) was left conform well to first-order kinetics. The observed first-order rate constant for the tautomerization, (**1**) → (**3**), was $1.7 \pm 0.2 \times 10^{-3}\ s^{-1}$ and the half-life of (**1**) in $CDCl_3$ in the presence of (**4**) (0.04 M) at 27 °C is *ca.* 7 min. A mixture of (**1**) (*ca.* 0.3 M) and (**3**) (*ca.* 0.9 M) in $CDCl_3$ could be separated from (**4**) at the later stage of the reaction using a dry ice–acetone trap. The rate of tautomerization of (**1**) to (**3**) in the absence of (**4**) is found to be significantly faster than in its presence. The half-life of (**1**) in the absence of (**4**) is estimated to be less than 4 min in $CDCl_3$ at 27 °C. It is certain that the enol (**1**) is stabilized by (**4**) in $CDCl_3$ and accordingly, the tautomerization of (**1**) to (**3**) is suppressed by (**4**).



(**2**) (**1**) (**3**) (1)

$[Rh(CO)(PPh_3)_3]ClO_4$

(**4**)

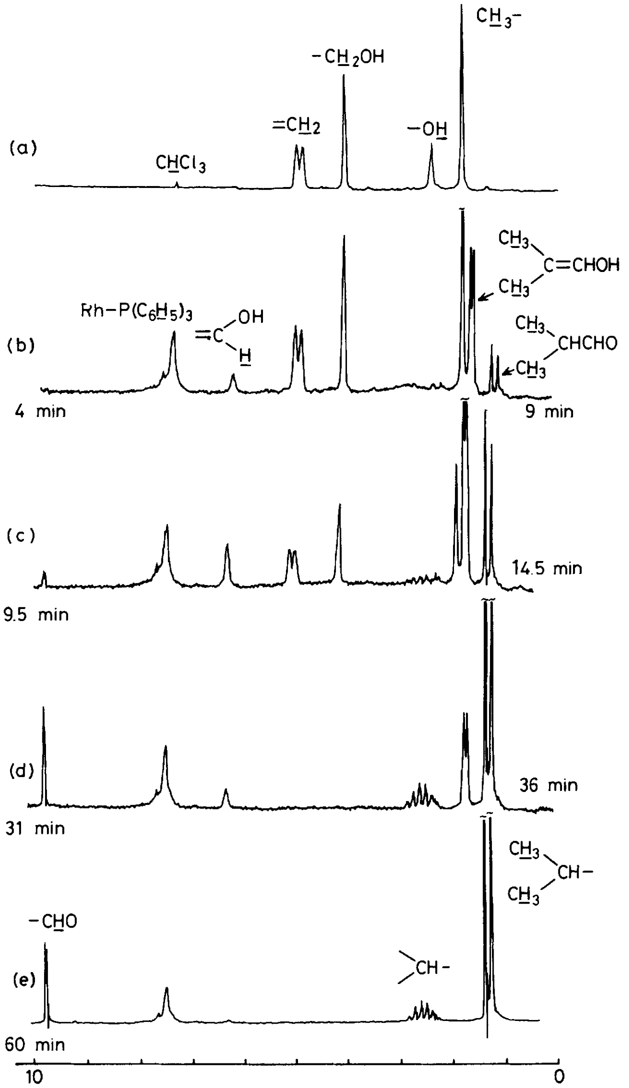


Figure 1. ^1H N.m.r. spectral changes during the isomerization of (**2**) (1.2 mmol) to (**3**) with $[Rh(CO)(PPh_3]ClO_4$ (**4**) (0.04 mmol) in $CDCl_3$ (1.0 cm^3) at 27 °C, under N_2, at 60 MHz. Scanning from δ 10 to 0 (relative to $SiMe_4$) took 5 min for each spectrum. (a) (**2**); (b) 4 min after addition of (**4**) into $CDCl_3$ solution of (**2**); spectrum shows no CHO signals of (**3**) but shows CH_3 signals of (**3**) since (**3**) was produced during the 5 min scanning time; (c) mixture of (**1**), (**2**), (**3**), and (**4**); (d) mixture of (**1**), (**3**), and (**4**); (e) mixture of (**3**) and (**4**).

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