# Generation of Simple Enols in Non-aqueous Solution by Fast Double-bond Migration of Allylic Alcohols with Rhodium(I) and Iridium(I) Complexes

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The complexes $[Rh(CO)(PPh_3)_3]ClO_4$ **1** and $[Ir(cod)(PhCN)(PPh_3)]ClO_4$ **2** (cod = cycloocta-1,5-diene), rapidly catalyse the double-bond migration of 2-ethylprop-2-en-1-ol **3** and prop-2-en-1-ol **4**, respectively to generate a significant amount of the enols 2-methylbut-1-en-1-ol **5** and prop-1-en-1-ol **6** in the absence of a solvent and in $CD_3COCD_3$. Both enols **5** and **6** are quite stable and slowly undergo ketonization to the corresponding carbonyl compounds at room temperature in the absence of a solvent and in aprotic solvents. Detailed $^1H$ NMR spectral data at 300 MHz suggest that two isomers (*Z* and *E*) of compound **5** are simultaneously produced in the reaction of **3** and **1**, the ratio of the isomers (major:minor) being *ca.* 6–9:1. Reaction of compound **4** with **2** also generates the *Z* (major) and *E* isomers (minor product) of **6**. The *Z* isomer initially generated rapidly undergoes isomerization to give the *E* isomer in the presence of **2**, while both the *Z* and *E* isomers relatively slowly undergo ketonization. Additional $^1H$ and $^{13}C$ NMR and infrared spectral data for $Me_2C{=}CHOD$ and $Me_2CDCHO$ are reported with some experimental details.

Following the excellent review on simple enols by Hart,[1] visible progress in studying enols has been made by the groups of Capon,[2] Kresge[3] and Rappoport.[4] Enols have been generated by various methods such as the hydrolysis of enol ethers,[2] photohydration of acetylenes,[3] hydrogenation and hydroarylation of ketenes,[4] and pyrolysis of bicyclo-unsaturated alcohols.[5] Recently, rapid catalytic double-bond migration of an allylic alcohol has been found to be another method of simple enol generation especially in the absence of a solvent or in aprotic solvents.[6] This enol generation is possible only with an appropriate catalyst which rapidly catalyses the double-bond migration of that particular allylic alcohol but does not (or very slowly) catalyses the ketonization of the enol produced in the preceding double-bond migration. We now report the preparation of two simple, aliphatic, and stable enols (one of which has never been reported even in aqueous solution) by fast double-bond migration of allylic alcohols with rhodium(I) and iridium(I) complexes in the absence of a solvent and in $CD_3COCD_3$. Detailed $^1H$ and $^{13}C$ NMR and IR spectral data for the previously reported enol, $Me_2C{=}CH(OD)$,[6] and its ketonization product, $Me_2CDCHO$, are also included in this report.

## Results and Discussion

Four-co-ordinated cationic $d^8$ metal complexes $[Rh(CO)(PPh_3)_3]ClO_4$ **1** and $[Ir(cod)(PhCN)(PPh_3)]ClO_4$ **2** (cod = cycloocta-1,5-diene),[7] have been found to be very effective catalysts for the double-bond migration of 2-ethylprop-2-en-1-ol **3** and prop-2-en-1-ol **4** respectively, to produce simple enols, 2-methylbut-1-en-1-ol **5** and prop-1-en-1-ol **6** [equations (1) and (2)]. The reaction rate of the deuteriated alcohol $CH_2{=}C(Et)CH_2OD$ **3D** with **1** to produce EtCMe=CHOD

$$\underset{\mathbf{3}}{CH_2{=}C(Et)CH_2OH} \xrightarrow[[Rh(CO)(PPh_3)_3]ClO_4\ \mathbf{1}]{\text{fast}} \underset{\mathbf{5}}{EtCMe{=}CHOH} \xrightarrow[\mathbf{1}]{\text{slow}} \underset{\mathbf{7}}{EtCHMeCHO} \quad (1)$$

$$\underset{\mathbf{4}}{CH_2{=}CHCH_2OH} \xrightarrow[[Ir(cod)(PhCN)(PPh_3)]ClO_4\ \mathbf{2}]{\text{fast}} \underset{\mathbf{6}}{MeCH{=}CHOH} \xrightarrow[\mathbf{2}]{\text{slow}} \underset{\mathbf{8}}{EtCHO} \quad (2)$$

**5D**, is practically equal to that of **3** with **1**, and ketonization of **5D** ($t_{\frac{1}{2}}$ = *ca.* 320 h at 25 °C in $CD_3COCD_3$) is much slower than that of **5** ($t_{\frac{1}{2}}$ = *ca.* 40 h at 25 °C in $CD_3COCD_3$). Complexes **1** and **2** also catalyse the ketonization of enols **5** and **6**, respectively to give the corresponding aldehydes. These reactions, however, are much slower than the double-bond migrations of **3** and **4**, respectively, and therefore a considerable amount of each enol (**5** and **6**) could be isolated from the catalysts **1** and **2**.

Double-bond migrations of 3-methylbut-1-ene and pent-1-ene with complexes **1** and **2** are much slower than those of compound **3** with **1** and of **4** with **2** under the same experimental conditions. Accordingly, the fast generation of **5** with **1** and of **6** with **2** may be understood by the effects of the OH groups of **3** and **4** which may interact with rhodium in **1** and iridium in **2**.

*2-Methylbut-1-en-1-ol* **5**.—Volatile materials, separated from the catalyst **1** in the reaction of compound **3** with **1** contained as high as 65% of the enol **5** (and 33% of the ketonization product, **7** and 2% of starting material **3**) (see Experimental section). A detailed $^1H$ NMR spectral investigation was carried out for **5** since this enol has never been reported. Signals of the enol **5** are readily distinguished from with those of compounds **3** and **7**. Proton NMR spectra also clearly show two isomers of the enol, **5a** (major component) and **5b** (minor component) (see below). The sharp doublet at δ 7.38 at 203 K shifts to 6.52 at 298 K (see Table 1) and the doublet also shifts from *ca.* δ 6.5 to 6.6 with varying concentration of **5**. The coupling constants measured and the integrals of the two doublets at δ 7.38 and 6.21 are equal, respectively. These observations enable us to assign the two doublets to OH (δ 7.38) and =C*H*(OH) (δ 6.21) of **5a**, respectively. These assignments are also supported by two-

**Table 1** Proton NMR data for 2-methylbut-1-en-1-ol **5** in $CD_3COCD_3$ at 298 K at 300 MHz

| Proton | Isomer | δ | *J*/Hz |
|---|---|---|---|
| $-CH_2CH_3$ | **5a** | 0.98 (t) | 7.5 ($-CH_2CH_3$) |
| | **5b** | *a* | |
| $-CH_2CH_3$ | **5a** | 2.12 (q) | 7.5 ($-CH_2CH_3$) |
| | **5b** | *a* | |
| $=C(C_2H_5)CH_3$ | **5a** | 1.52 (d) | 1.5 ($HC=CCH_3$) |
| | **5b** | 1.60 (d) | 1.5 ($HC=CCH_3$) |
| =CH(OH) | **5a** | 6.21 (d)[b] | *c* |
| | | | 6.0 (=CHOH)[d] |
| | **5b** | 6.25 (d)[e] | 1.5 ($HC=CCH_3$) |
| | | | 6.0 (=CHOH)[d] |
| =CH(OH) | **5a** | 6.52 (d)[f] | 6.0 (=CHOH)[d] |
| | **5b** | 6.53 (d)[f] | 6.0 (=CHOH)[d] |

[a] Not distinguished from the signals of compound **5a**. [b] Multiplet in resolution-enhanced spectrum in Fig. 3. [c] Not resolved clearly (see Fig. 3). [d] Decreases with decreasing temperature: 6.0 Hz at 298–273, 5.2 Hz at 243–203 K. [e] Two quartets in resolution-enhanced spectrum in Fig. 3. [f] Shifts from δ 6.5 to 6.6 with varying concentration of compound **5** and from δ 6.5 at 298 K to δ 7.4 at 203 K.

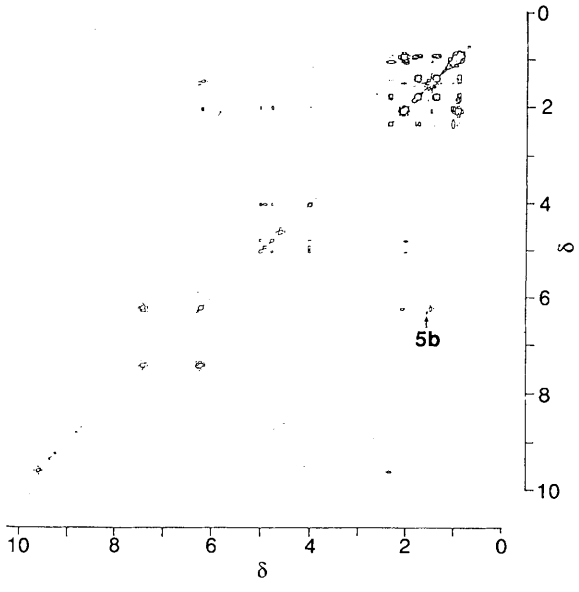



**Fig. 1** Two-dimensional COSY $^1H$ NMR spectrum of the mixture of $CH_2=C(Et)CH_2OH$ **3**, EtCMe=CHOH **5a**, **5b** and EtCHMeCHO **7** at 300 MHz in $CD_3COCD_3$ at 203 K

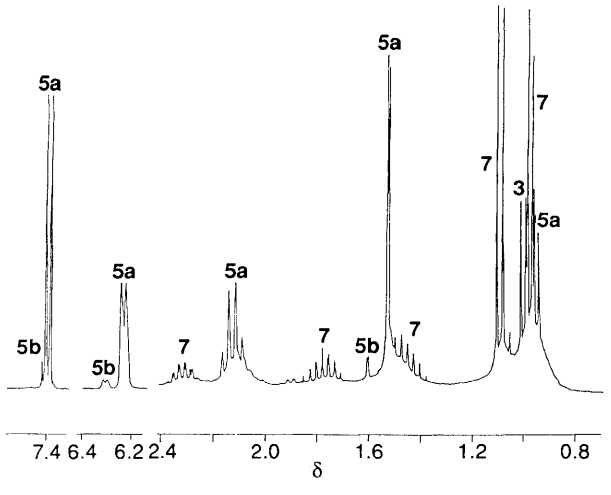



**Fig. 2** High-resolution $^1H$ NMR spectrum of the mixture of compounds **3**, **5a**, **5b** and **7** at 300 MHz in $CD_3COCD_3$ at 203 K

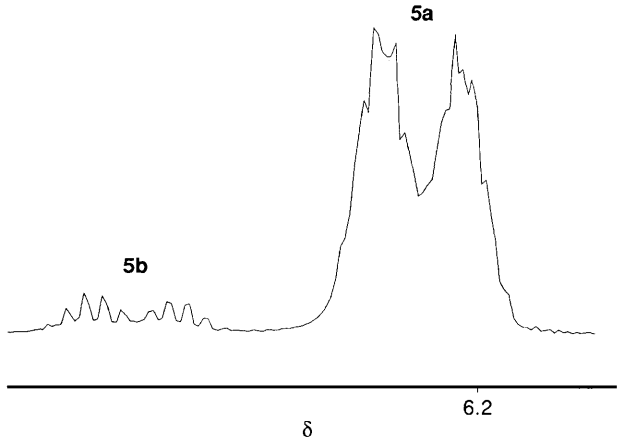
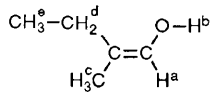
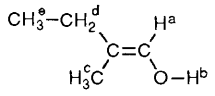



**Fig. 3** Resolution-enhanced $^1H$ NMR spectrum for the region of =CHOH of compounds **5a** and **5b** at 300 MHz in $CD_3COCD_3$ at 203 K




(*Z*)-**5**




(*E*)-**5**

dimensional correlation spectroscopy (COSY) (Fig. 1 showing apparent coupling between the signals at δ 7.38 and 6.21. The rest of the assignments are rather straightforward as given in Table 1.

Another set of small signals always appear near to each signal of compound **5a**: doublets at δ 1.60 (near to 1.52 of **5a**) due to $=CCH_3$, δ 6.25 (near to 6.21 of **5a**) due to =CH(O*H*), and δ 7.40 (near to 7.38 of **5a**) due to =CH(O*H*) (Fig. 2). These small signals are assigned to the corresponding protons of the other isomer of the enol, **5b** (see also Table 1). The signals due to $-CH_2CH_3$ and $-CH_2CH_3$ of **5b** are not resolved clearly from those of **5a**, although some broadening of the signals of **5a** near to the baseline has been observed in high-resolution spectra. It should be mentioned that no evidence has been obtained for isomerization between **5a** and **5b** during the ketonization to give **7** in the absence and presence of **1**.

Resolution-enhanced $^1H$ NMR spectral data for the OH region have been used to determine the ratio of *E* and *Z* isomers of simple enols.[8] Further splitting of the doublet due to OH was not observed even in the resolution-enhanced spectrum of **5**. The two doublets at δ 6.21 of **5a** and δ 6.25 of **5b** due to =C*H*(OH), however, are further split into two multiplets at δ 6.21 and two quartets at δ 6.25, respectively, as shown in Fig. 3. These splittings are evidently due to long-range couplings of $H^a$ with $H^c$ and $H^d$ (and possibly with $H^e$). The two quartets of **5b** at δ 6.25 in Fig. 3 seem to be result of the coupling between $H^a$ and $H^c$. The two-dimensional COSY $^1H$ NMR spectrum (Fig. 1) clearly shows the coupling between $H^a$ (δ 6.25) and $H^c$ (δ 1.60) of **5b**. The two multiplets at δ 6.21 of **5a** can not be understood by a single coupling between $H^a$ and $H^c$ or $H^d$. The two-dimensional COSY $^1H$ NMR spectrum clearly shows the couplings of $H^a$ at δ 6.21 wtih $H^c$ at δ 1.52 and $H^d$ at δ 2.12. In short, both couplings of $H^a$ with $H^c$ and $H^d$ are observed for **5a** while only the coupling of $H^a$ with $H^c$ is seen for **5b**. These observations still do not lead us to identify **5b** (or **5a**) as (*E*)- or (*Z*)-**5** since the coupling constants between $H^a$ and $H^c$ in (*E*)- and (*Z*)-**5** are practically equal.[9]

Reaction of deuteriated 2-ethylprop-2-en-1-ol **3D** $CH_2=C(Et)CH_2OD$, with **1** gives the deuteriated enol EtCMe=CHOD **5D** whose $^1H$ NMR data are in good agreement with the assignments made above. The spectrum of the reaction mixture obtained in the reaction of **3D** (containing *ca.* 15% of non-deuteriated starting material **3**) with **1** shows only singlets at δ 6.21 and 6.25 due to =C*H*OD of **5a** and **5b** respectively and a

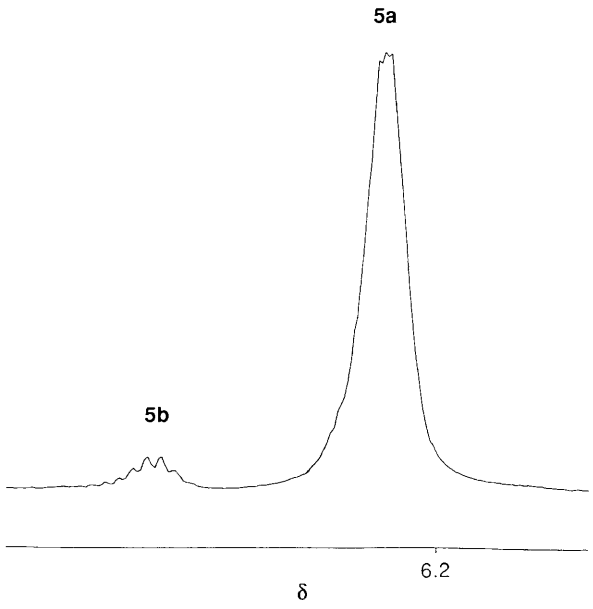



**Fig. 4** Resolution-enhanced $^1$H NMR spectrum for the region of =CHOD of EtCMe=CHOD, deuteriated **5a** and **5b**, at 300 MHz in $CD_3COCD_3$ at 203 K

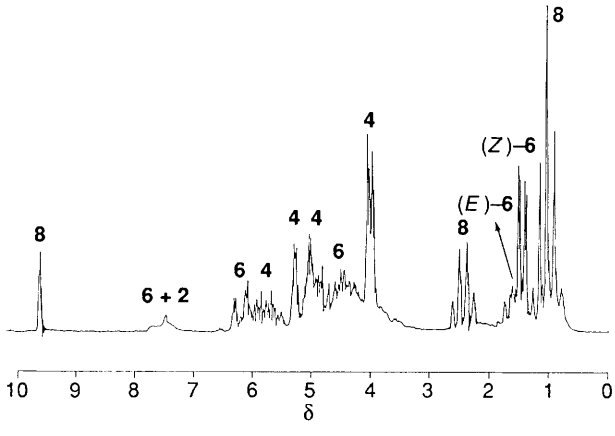



**Fig. 5** Proton NMR spectrum of a mixture of $CH_2$=$CHCH_2OH$ **4**, (*Z*)-MeCH=CHOH (*Z*)-**6**, (*E*)-MeCH=CHOH (*E*)-**6**, EtCHO **8**, and $[Ir(cod)(PhCN)(PPh_3)]ClO_4$ **2** in $CD_3COCD_3$ at 60 MHz at 298 K

weak (*ca.* one sixth of =C*H*OD signals) doublet due to OH of non-deuteriated **5**.

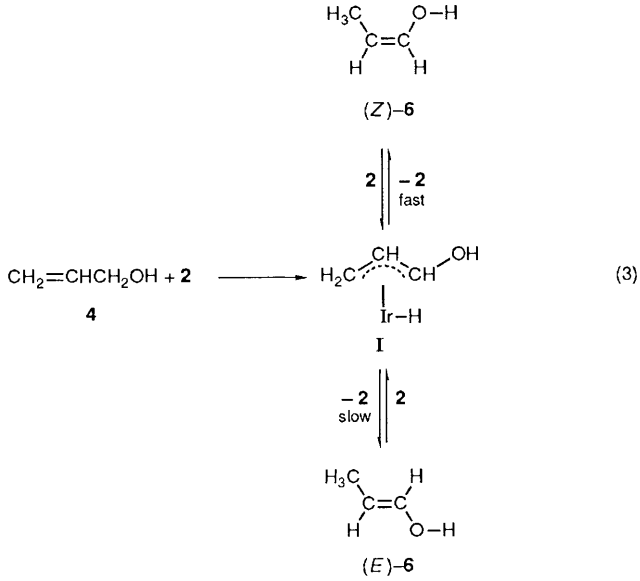
One may expect to obtain valuable information, possibly from the better resolution of =C*H*OH signals in the resolution-enhanced $^1$H NMR spectra for determining the structures of isomers **5a** and **5b**, by replacing the hydroxyl hydrogen of **5** with deuterium. The resolution-enhanced spectrum of **5D** (85% D) for $H^a$ (=C*H*OD) region shows a quartet at δ 6.25 and a poorly resolved multiplet at δ 6.21 (Fig. 4). As expected, the two quartets at δ 6.25 of **5b** merge into a quartet (due to coupling between $H^a$ and $H^c$ of deuteriated **5b** replacing OH with OD. Weak signals due to the non-deuteriated enol **5b** (15%) are also seen around the quartet in Fig. 4. The multiplet at δ 6.21 for deuteriated **5a** in Fig. 4 in place of two multiplets for **5a** is apparently due to the couplings of $H^a$ with $H^c$ and $H^d$ and is poorly resolved probably due to the signals of non-deuteriated enol **5a** at the bottom of the multiplet. Unfortunately, even the resolution-enhanced $^1$H NMR measurements for **5D** at 300 MHz at 203–298 K do not provide conclusive information to determine the structures of **5a** and **5b**.

The temperature dependence of the coupling constant, *J* (=CHOH) for simple enols has been observed and understood in terms of an equilibrium between two conformers (*syn* and *anti*).[10] The corresponding coupling constant, of compound **5a** decreases from 6.0 Hz at 298 K to 5.2 Hz at 203 K, which may also be understood in terms of an equilibrium between the syn (more stable) and anti conformers (less stable). It is interesting that *J*(=CHOH) of (*Z*) prop-1-en-1-ol decreases with decreasing temperature while that of (*E*)-prop-1-en-1-ol increases.[10b] Increases in chemical shifts of hydroxyl hydrogens of simple enols with decreasing temperature were interpreted as the enol–solvent interaction.[10b] The chemical shift of OH of compound **5** (of same concentration) also shifts from δ 6.52 at 298 K to δ 7.38 at 203 K.

The enol **5** is quite stable in the absence of a solvent as well as in aprotic solvents when the catalyst, **1** is removed from the reaction mixture. It slowly undergoes ketonization in the absence of a solvent ($t_{\frac{1}{2}}$ = *ca.* 40 h) and in aprotic solvents such as $CD_3COCD_3$ ($t_{\frac{1}{2}}$ = *ca.* 40 h) and $C_6D_6$ ($t_{\frac{1}{2}}$ = *ca.* 24 h) at room temperature. These ketonization rates are comparable with those of 2-methylprop-1-en-1-ol.[6] In the absence of a solvent or in $CD_3OD$, the enol, **5** also gives considerable amounts of aldol condensation products as observed for 2-methylprop-1-en-1-ol.[6]

*Prop*-1-*en*-1-*ol* **6**.—This enol was generated and studied in detail in aqueous solution[10a,11] but has never been reported in non-aqueous solution. It is very interesting to find that the iridium(I) complex **2** is a very effective catalyst for the isomerization of allyl alcohol **4** to generate the simple enol **6** in the absence of a solvent as well as in $CD_3COCD_3$ [equation (2)] while no enol **5** was observed in the reaction of **4** with the rhodium(I) complex **1**. Effective generation of enols could be achieved by catalytic double-bond migration of allylic alcohols by a metal complex that rapidly catalyses the migration but does not (or very slowly) catalyse ketonization of the enol. But-3-en-2-ol rapidly undergoes isomerization to give butan-2-one in the presence of $[Ir(ClO_4)(CO)(PPh_3)_2]$ with no observable amount of but-2-en-2-ol because the ketonization of the enol is also rapidly catalysed by the iridium(I) complex.[12]

Both (*Z*)- and (*E*)-prop-1-en-1-ol, **6**, were generated from the corresponding precursors, respectively and their detailed $^1$H NMR spectral data reported.[10a,11] The isomerization between (*Z*)- and (*E*)-**6** [equation (3)] has not been reported. By comparing the $^1$H NMR spectrum of the reaction mixture of compounds **4** and **2** (Fig. 5) with the data reported for (*Z*)- and (*E*)-**6**,[10a] it is readily understood that the reaction generates the enol **6**: mostly the *Z* isomer (doublet of doublets at δ 1.41 due to $CH_3$[10a]) and a small amount of the *E*-isomer (doublet of doublets; at δ 1.44 due to $CH_3$[10a]). Fig. 6 shows that the signals of (*E*)-**6** increase at the expense of those of (*Z*)-**6** in the presence of compound **2**. This catalytic isomerization (Fig. 6) was



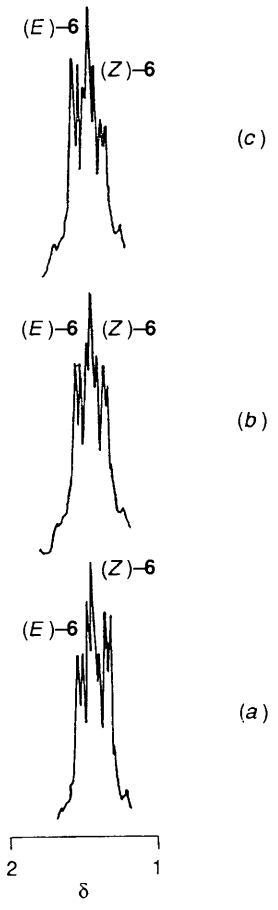



**Fig. 6** Proton NMR spectral changes for the region of $CH_3$ of MeCH=CHOH **6** showing increases of (*E*)-**6** at the expense of (*Z*)-**6** in the presence of $[Ir(cod)(PhCN)(PPh_3)]ClO_4$ **2** in $CD_3COCD_3$ at 60 MHz. Spectra (*a*)–(*c*) were measured at intervals of 1 min at 298 K

measured after the starting material, **4** had disappeared completely in the reaction mixture from which no more enol **6** could be generated. Complex **2** also catalyses the ketonization of both (*Z*)- and (*E*)-**6** to give propanal, **8** [equation (2)]: ketonization of the enol **6** is somewhat (but not much) faster in the presence of **2** than in its absence.

When $CD_3COCD_3$ is used as a solvent a significant amount (up to 60%) of compound **6** could be obtained while relatively less, (up to 40%) was observed in the absence of a solvent (see Experimental section). Enol **6** is also quite stable and slowly undergoes ketonization ($t_{\frac{1}{2}}$ = *ca.* 15 h) in the absence of **2** in $CD_3COCD_3$ at room temperature. Observable amounts of non-volatile oligomers were also seen at the end of the reaction.

Both double-bond migrations of compound **3** with **1** and of **4** with **2** would most likely involve a 1,3-hydrogen shift reaction of **3** and **4** through a π-allylhydridometal intermediate, **I**.[13] Equilibria between the intermediate **I** and (*Z*)- and (*E*)-**6** [equation (3)] may explain the initial formation of (*Z*)-**6** as a kinetic product which in part undergoes isomerization through **I** to (*E*)-**6** to give a thermodynamic mixture of (*Z*)- and (*E*)-**6**. Elimination of (*Z*)-**6** from **I** would occur in such a way that the interaction of (*Z*)-**6** with iridium in **2** exercises the least steric hindrance: bulky $PPh_3$, cod, and possibly $ClO_4$ ligands around iridium in **2** may push both of the methyl and hydroxyl groups of **6** away.

Since a previous report[6] some additional data have been

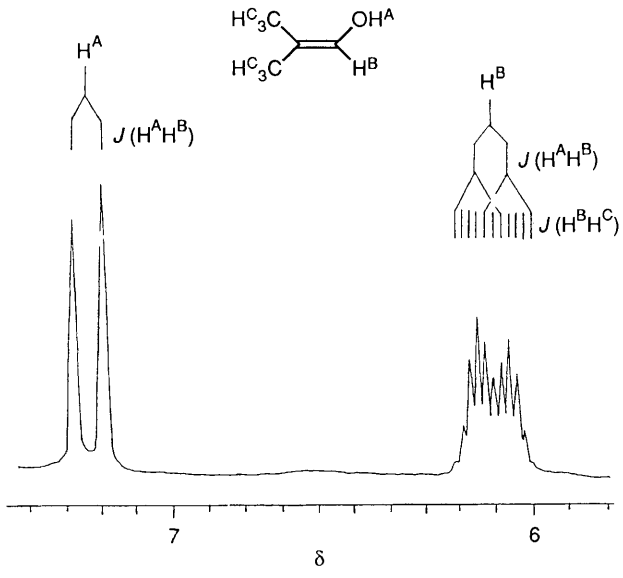



**Fig. 7** High-resolution $^1H$ NMR spectra of MeC=CHOH in the region of =CH and =CHOH at 80 MHz at 228 K in $CD_3COCD_3$

obtained for the enols $Me_2C$=CHOH **9** and $Me_2C$=CHOD, **9D**, and the ketonization product of **9D**, $Me_2CDCHO$, **10D**. The high-resolution $^1H$ NMR spectrum of **9** shows 11 lines due to =C*H*OH from which the couplings of =CH with OH ($J$ = 5.5 Hz) and $Me_2C$= ($J$ = 1.3 Hz) are apparent (see Fig. 7). Both $^1H$ and $^{13}C$ NMR and IR spectral data clearly confirm the presence of **9D** and **10D** (see spectral data and experimental details in Experimental section).

## Experimental

NMR spectra were recorded on a Bruker WH-300 pulsed FT spectrometer at 300 MHz for enol **5** (and **3** and **7**), a Varian EM-360A spectrometer at 60 MHz for enol **6** (and **4** and **8**), and a Bruker WP 80 MHz FT spectrometer at 80 MHz for **9**. The catalyst $[Rh(CO)(PPh_3)_3]ClO_4$ **1**[14] was prepared by the known method. Allyl alcohol **4** and 2-methylprop-2-en-1-ol were purchased from Aldrich (24,053-2) and Fluka (64220), respectively and used without further purification.

*Preparations.*—$[Ir(cod)(PhCN)(PPh_3)]ClO_4$ **2**. Silver perchlorate (0.038 g, 0.18 mmol) was added to a $CH_2Cl_2$ (5 $cm^3$) solution of $[IrCl(cod)(PPh_3)]$ (0.11 g, 0.18 mmol) in the presence of one drop of PhCN under nitrogen at room temperature and the reaction mixture was stirred for 30 min until a significant amount of white precipitate (AgCl) was seen in a clear red solution. Addition of hexane (10 $cm^3$), after removal of AgCl by filtration, resulted in precipitation of red microcrystals (90%) of $[Ir(cod)(PhCN)(PPh_3)]ClO_4$ **2**. $^1H$ NMR ($CDCl_3$): δ 7.40 (m, $C_6H_5$) and 2.8–1.3 (m, all protons of cod). IR (Nujol): $\nu_{max}$/$cm^{-1}$ 2240w (C≡N) and 1100s ($ClO_4$). $\Lambda_M$ = 50 $\Omega^{-1}$ $cm^2$ $mol^{-1}$ ([Ir] = 2 × $10^{-5}$ mol $dm^{-3}$) in $CH_2Cl_2$ at 25 °C (*cf.* 53 $\Omega^{-1}$ $cm^2$ $mol^{-1}$ for $NBuClO_4$) (Found: C, 51.6; H, 4.25; N, 1.85. Calc. for $C_{33}H_{32}IrNP$: C, 51.8; H, 4.20; N, 1.85%).

2-*Ethylprop*-2-*en*-1-*ol* **3**. Lithium aluminium hydride* (0.4 g, *ca.* 10 mmol) (Fluka 62420) was added to a tetrahydrofuran (thf) solution (80 $cm^3$) of 2-ethylacrolein (3.4 g, *ca.* 40 mmol; Fluka 02843) in an ice-bath and the reaction mixture was stirred for 2.5 h before water (100 $cm^3$) was added. The product was extracted with diethyl ether (100 $cm^3$) three times and dried with anhydrous $MgSO_4$ which was then removed by filtration. Diethyl ether and thf were removed by vacuum pumping and the residue was distilled at 132 °C to obtain 2.4 g of compound **3**.† NMR: $^1H$ ($CD_3COCD_3$), δ 1.05 (t, $CH_3$), 2.07 (q, $CH_2CH_3$), 3.89 (t, OH), 4.03 (d, $CH_2OH$), 4.80 (m, $=CH_2$, Hα) and 5.01 (m,

* An effective reagent for the hydrogenation of unsaturated aldehydes to unsaturated alcohols.

† 2-Ethylprop-2-en-1-ol was reported very briefly (b.p. 133 °C) with no spectral data.

$=CH_2$, Hβ); $^{13}C$ ($CDCl_3$, 25 °C), δ 11.94 ($CH_3$), 25.48 ($CH_2CH_3$), 65.50 ($CH_2OH$), 107.70 [$(CH_3)_2C=$], and 150.50 ppm (=CHOH) IR (neat): $\nu_{max}/cm^{-1}$ 3300s (br) (O–H), 1660m, (C=C) and 1220w (C–O).

*Compound* **3D**. A mixture of compound **3** (10 g) and $D_2O$ (20 $cm^3$) was stirred for 30 min and the organic layer was separated using a separatory funnel. The same procedure was repeated three times more before anhydrous $MgSO_4$ was added to remove $D_2O$, HDO and $H_2O$ in the organic layer. Distillation at 135 °C gave $CH_2$=C(Et)$CH_2$OD, **3D**, whose proton NMR spectrum indicated that *ca.* 85% of the hydroxyl hydrogen of **3** had been replaced with deuterium.

2-*Methylbut*-1-*en*-1-*ol* **5**. Addition of [Rh(CO)$(PPh_3)_3$]-$ClO_4$ **1** (20 mg, 0.02 mmol), to compound **3** (1 $cm^3$, 12 mmol) in an NMR tube under nitrogen at room temperature immediately initiated an exothermic reaction. The warm-hot reaction mixture was kept at 0 °C for *ca.* 30 min until most of **3** had disappeared (decrease of the doublet due to $CH_2OH$ of **3** at δ 4.03). Volatile materials (*ca.* 0.8 $cm^3$) were separated from the catalyst **1** using a solid $CO_2$–acetone trap, yielding *ca.* 65% of the enol **5**, 33% of the final product 2-methylbutanal, **7** and 2% of the starting material **3** according to the proton NMR spectrum (see Table 1 and text).

EtCMe=CHOD **5D**. This enol was prepared in the same manner as described for **5** using complex **1**, (20 mg, 0.02 mmol) and **3D** (1 $cm^3$, 12 mmol) containing *ca.* 15% of **3**. The $^1H$ NMR spectrum of the volatile materials (*ca.* 0.7 $cm^3$) separated from the catalyst **1** clearly showed singlets at δ 9.63 due to CHO of EtCDMeCHO **7D**, and δ 6.21 due to =CHOD of **5D** in $CD_3COCD_3$. A weak doublet at *ca.* δ 7.20 due to OH of non-deuteriated enol **5** was also observed. Integrals of the signals at δ 6.21, 9.63, and 7.20 indicated that the products contain 72% of **5D**, 17% of **7D** (and possibly a small amount of **7**), and 11% of **5**.

*Prop*-1-*en*-1-*ol*, **6** *in the absence of a solvent*. The complex [Ir(cod)(PhCN)$(PPh_3)$]$ClO_4$ **2** (15 mg, 0.02 mmol) was added to cold prop-2-en-1-ol, **4** (0.85 $cm^3$, 12.5 mmol) at −20 °C in a NMR tube in an ice–NaCl bath. The violent exothermic isomerization immediately began to warm the reaction mixture which was thus taken out of the bath and put in another one maintained at 5–8 °C. (No enol **6** was observed when **2** was added **4** at room temperature probably because the reaction produces so much heat that the following ketonization becomes too fast to show **6** in the reaction mixture.) Repetitive proton NMR measurements showed generation of the enol **6** which undergoes ketonization to give **8**. The generation of **6** was followed by measuring the $^1H$ NMR signals due to $CH_3$ of (*Z*)-**6** at δ 1.41 (dd) and of (*E*)-**6** at δ 1.44 (dd).[10a] Other signals were also clearly seen at δ 6.0–7.0 [two broad OH signals for (*Z*)- and (*E*)-**6**], 6.20–6.40 [m, =C*H*OH for (*Z*)- and (*E*)-**6**], and 4.50 [m, =CHMe for (*E*)-**6**][10a] with =CHMe signals for (*Z*)-**6** not being resolved due to large signals from the remaining **4** and oligomers produced at the end of the reaction. The remaining starting material **4** and final product **8** were identified by the C*H*$_2$(OH) signal of **4** at δ 4.10(m) and CHO signal of **8** at δ 9.70 (t), respectively. Most of compound **4** disappeared within 90 min by which time a significant amount of **6** (*ca.* 20%) was still present in the reaction mixture. The maximum concentration of enol **6** (*ca.* 40%) was observed 15 min after mixing of **2** and **4**.

*Prop*-1-*en*-1-*ol in* $CD_3COCD_3$. Complex **2** (15 mg, 0.02 mmol) was added to a cold mixture of **4** (0.3 $cm^3$, 4.0 mmol) and $CD_3COCD_3$ (0.5 $cm^3$) at −20 °C in a NMR tube in an ice–NaCl bath. Exothermic isomerization was immediately initiated, warming the reaction mixture which was then taken out of the bath and put into another maintained at 5–8 °C. Analyses of compounds **4**, **6**, and **8** in the reaction mixture were carried out by measuring $^1H$ NMR spectra at intervals of 3 min as described above. The maximum concentration of **6** (60%) was obtained within 1 h at which time the volatile materials (*ca.* 0.6 $cm^3$) were separated from non-volatile materials (iridium catalyst and very small amount of oligomers) by using a solid $CO_2$–acetone trap. The $^1H$ NMR spectrum of the volatile materials showed that they contained *ca.* 50% of **6** (*Z*:*E* = *ca.* 4:1, 45% of **8**, and 5% of **4**. The enol, **6** is much more stable ($t_{\frac{1}{2}}$ = 15 h) in $CD_3COCD_3$ in the absence of the iridium(I) catalyst **2** than in its presence ($t_{\frac{1}{2}}$ = 1 h). Isomerization of (*Z*)- to (*E*)-**6** was not observed in the absence of **2**.

*Compound* **11D**. This compound was prepared in the same manner as described for **3D**. The $^1H$ NMR spectrum of the product showed that more than 97% of the hydroxyl hydrogen of 2-methylprop-2-en-1-ol **11** was usually replaced by deuterium to give $CH_2$=C(Me)$CH_2$OD, **11D**.

2-*Methylprop*-1-*en*-1-*ol* **9**. Complex **1** (20 mg, 0.02 mmol) was added to compound **11** (1 $cm^3$, 13 mmol) under nitrogen at room temperature to initiate exothermic isomerization of **11** to **9**. The warm-hot reaction mixture was immediately cooled in an ice-bath at 0 °C for 1 h until most of **11** had disappeared according to $^1H$ NMR measurements. Volatile materials (0.8 $cm^3$), separated from the catalyst, **1** by a solid $CO_2$–acetone trap, contained 90–95% of **9** and 5–10% of 2-methylpropanal. NMR ($CD_3COCD_3$) of **9**: $^1H$ (−47 °C), δ 1.48 (d, $CH_3$), 6.11 (m, =C*H*OH) and 7.25 (d, OH, see Fig. 8). $^{13}C$ (25 °C), δ 135.25 (=CHOH), 107.05 (*C*=CHOH), 18.95, and 14.85 ppm ($CH_3$) IR (neat): $\nu_{max}/cm^{-1}$ 3400br (O-H), 1690s (C=C) and 1140br (C–O). Electronic absorption: $\lambda_{max}/nm$ 205 (in water) and 210 (in MeOH).

MeC=CHOD **9D**. This deuteriated enol was generated in the same manner as described for **9** using **11D** (1 $cm^3$) and **1** (20 mg) to obtain 0.8 $cm^3$ of volatile materials containing more than 95% of **9D**. NMR ($CD_3COCD_3$, 25 °C): $^1H$, δ 1.53 (d, $CH_3$) and 6.24 (s, =C*H*OH); $^{13}C$ δ 136.06 (=CHOH), 106.52 (*C*=CHOH), 15.45, and 14.35 ppm ($CH_3$). IR (neat): $\nu_{max}/cm^{-1}$ 2500s (O-D), 1680m (C=C) and 1140s (C–O).

$Me_2$CDCHO **10D**. A portion (0.8 $cm^3$) of the volatile materials containing *ca.* 95% of **9D**, obtained in the above reaction, was kept at 40 °C for 3 h until most **9D** had disappeared ($^1H$ NMR signed of =CHOD at δ 6.24). As was observed for $Me_2C$=CHOH in the absence of a solvent,[6] the reaction mixture produced a significant amount of unknown products which are much less volatile than **10D**. About 0.5 $cm^3$ of $Me_2$CHCHO **10D** was obtained by vacuum distillation at room temperature using a solid $CO_2$–acetone trap. NMR ($CD_3COCD_3$): $^1H$ (25 °C), δ 1.10 (s, $CH_3$) and 9.65 (s, CHO); $^{13}C$ (−45 °C), δ 207.01 (CO), *ca.* 29.5 ($Me_2$*C*D, overlapped with $CH_3COCH_3$ signals), and 15–12 ppm ($CH_3$). IR (neat): $\nu_{max}/cm^{-1}$ 2140w, 2320w (C–D) and 1730s (C=O).

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