

$\delta$  3.86 and 3.68 ppm while the disubstituted Cp ring gives rise to five broad signals expected for the ABC protons. The methine proton appears as a quartet at  $\delta$  4.26 ppm as usual.

Obviously, much work has yet to be done concerning the mechanisms for the formation of these unexpected phosphine oxides not alone their further uses as ligands for the preparation of other series of coordination compounds. The compound **5** is also interesting in that it may be used not only in the synthesis of heteronuclear metal clusters but also in homogeneous catalytic cyclization of some alkynes. These points are the subject of our future communication.

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- For **2**:  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61-7.39(m,  $\text{C}_6\text{H}_5$ ), 4.72(b,  $\text{C}_5\text{H}_4$ ), 4.26(b,  $\text{C}_5\text{H}_5$ ).  $^{31}\text{P-NMR}$  (121.5 MHz,  $\text{CDCl}_3$ )  $\delta$  26.13 (s). Anal. Calcd for  $\text{C}_{22}\text{H}_{19}\text{POFe}$ : C, 68.42; H, 4.92. Found: C, 67.90; H, 4.70. For **3**:  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64-7.37(m,  $\text{P(O)Ph}_2$ ), 7.27(b,  $\text{PPh}_2$ ), 4.57 and 4.36(b,  $\text{C}_5\text{H}_4\text{P(O)Ph}_2$ ), 4.21 and 4.03(b,  $\text{C}_5\text{H}_4\text{PPh}_2$ ).  $^{31}\text{P-NMR}$  (121.5 MHz,  $\text{CDCl}_3$ )  $\delta$  6.72 (s,  $\text{P(O)Ph}_2$ ), -19.37(s,  $\text{PPh}_2$ ). Anal. Calcd for  $\text{C}_{34}\text{H}_{28}\text{P}_2\text{OFe}$ : C, 71.59; H, 4.91. Found: C, 70.70; H, 4.74.
- Crystal data for **2**: Space group  $\text{P2}_1/\text{c}$ ,  $a=14.172(2)$ ,  $b=10.434(1)$ ,  $c=11.894(2)$  Å,  $\beta=90.53(1)^\circ$ ,  $V=1758.7(5)$  Å<sup>3</sup>,  $Z=4$ ,  $D_{\text{calcd}}=1.494$  gcm<sup>-3</sup>, Mo-K $\alpha$  radiation,  $\lambda=0.71073$  Å,  $\mu=2.29$  cm<sup>-1</sup>. An Enraf-Nonius CAD-4 diffractometer, 2047 unique absorption corrected reflections with  $1>3\sigma$  (1) in the range  $3^\circ < 2\theta < 50^\circ$ . The structure was solved by Patterson and Fourier Methods. Final  $R=0.0317$ ,  $R_w=0.0374$ .
- For **4**:  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65-7.32 (m,  $\text{C}_6\text{H}_5$ ), 4.41-4.25(m,  $\text{C}_5\text{H}_3$ ), 4.18(s,  $\text{C}_5\text{H}_5$ ), 3.89(q,  $^3J=6$  Hz, CH), 1.63(s,  $\text{NMe}_2$ ), 1.15(d,  $^3J=6$  Hz,  $\text{CMe}$ ).  $^{31}\text{P-NMR}$  (121.5 MHz,  $\text{CDCl}_3$ )  $\delta$  25.03 (s). Anal. Calcd for  $\text{C}_{26}\text{H}_{28}\text{NPOFe}$ : C, 68.29; H, 6.13; N, 3.06. Found: C, 68.10; H, 6.18; N, 3.15.
- Crystal data for **4**: space group  $\text{P2}_1$ ,  $a=9.3252(8)$ ,  $b=11.342(1)$ ,  $c=11.043(1)$  Å,  $\beta=102.631(8)^\circ$ ,  $V=1139.8(2)$  Å<sup>3</sup>,  $Z=2$ ,  $D_{\text{calcd}}=1.331$  gcm<sup>-3</sup>, Mo-K $\alpha$  radiation,  $\lambda=0.71073$  Å,  $\mu=2.29$  cm<sup>-1</sup>. An Enraf-Nonius CAD-4 diffractometer, 1797 unique absorption corrected reflections with  $1>3\sigma$  (1) in the range  $3^\circ < 2\theta < 50^\circ$ . The structure was solved by Patterson and Fourier Methods. Final  $R=0.0311$ ,  $R_w=0.0344$ .
- For **5**:  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59-7.14(m,  $\text{C}_6\text{H}_5$ ), 4.36-4.13(m,  $\text{C}_5\text{H}_3$ ), 3.92(s,  $\text{C}_5\text{H}_5$ ), 3.84(q,  $^3J=6$  Hz, CH), 1.76(s,  $\text{NMe}_2$ ), 1.23(d,  $^3J=6$  Hz,  $\text{CMe}$ ).  $^{31}\text{P-NMR}$  (121.5 MHz,  $\text{CDCl}_3$ )  $\delta$  26.64(s,  $\text{PPh}_2\text{Co}$ ), -25.82(s,  $\text{PPh}_2$ ). Anal. Calcd for  $\text{C}_{81}\text{H}_{79}\text{N}_2\text{P}_4\text{Fe}_2\text{Co}$ : C, 70.76; H, 5.75; N, 2.04. Found: C, 70.30; H, 5.51; N, 2.15.
- For **6**:  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55-7.32(m,  $\text{C}_6\text{H}_5$ ), 4.81, 4.73, 4.59, 4.52 and 4.47(b,  $\text{C}_5\text{H}_3$ ), 4.26(q,  $^3J=9$  Hz, CH), 3.86 and 3.68 (b,  $\text{C}_5\text{H}_4$ ), 1.56(s,  $\text{NMe}_2$ ), 1.01(d,  $^3J=9$  Hz,  $\text{CMe}$ ).  $^{31}\text{P-NMR}$  (121.5 MHz,  $\text{CDCl}_3$ )  $\delta$  26.17(s), 23.78 (s). Anal. Calcd for  $\text{C}_{38}\text{H}_{37}\text{NP}_2\text{O}_2\text{Fe}$ : C, 67.97; H, 5.51; N, 2.08. Found: C, 67.90; H, 5.61; N, 1.87.

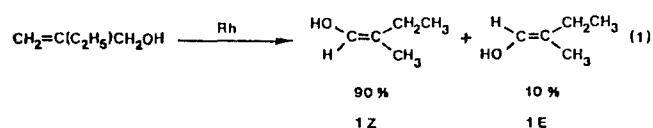
## Determination of Z-and E-2-Methylbut-1-en-1-ol

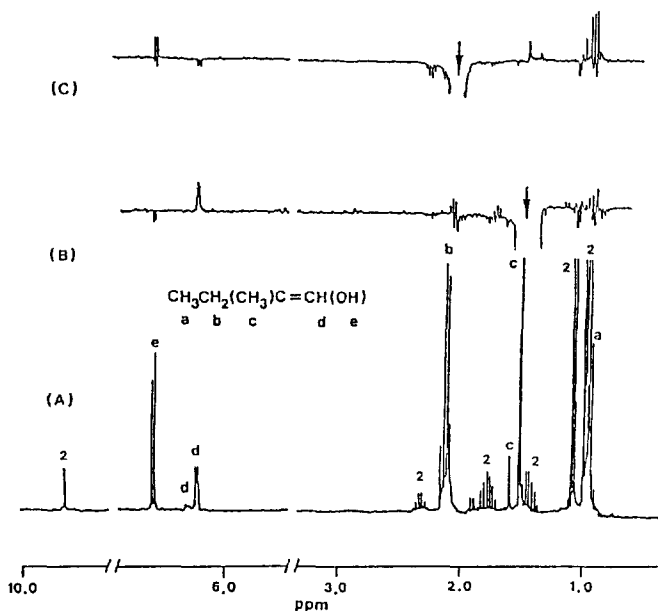
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Fast double bond migration of allylic alcohols with metal complexes is an unique way of generating simple enols in non-aqueous solvents.<sup>1,2</sup> The reaction of 2-ethylprop-2-en-1-ol with  $[\text{Rh}(\text{CO})(\text{PPh}_3)_3] \text{ClO}_4$  generates a simple and relatively stable enol, 2-methylbut-1-en-1-ol, **1** containing both **Z**- and **E**-isomers according to  $^1\text{H-NMR}$  data (Eq. 1).<sup>2</sup> Unambiguous assignments of the  $^1\text{H-NMR}$  signals of **1**, however,



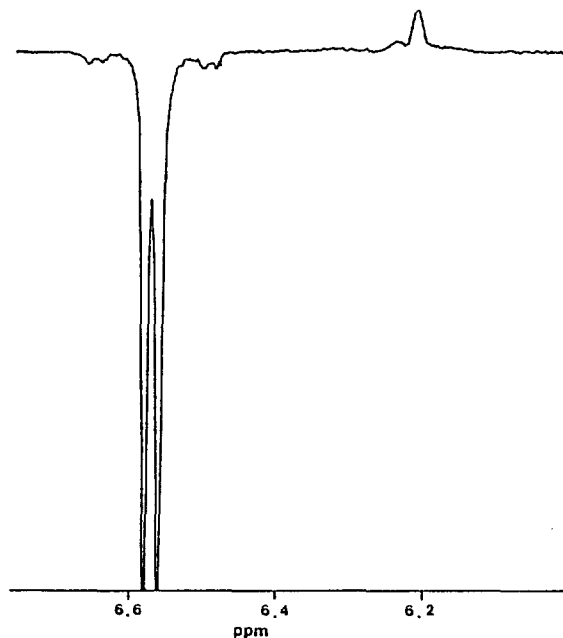


**Figure 1.** (A)  $^1\text{H-NMR}$  spectrum of the mixture of 2-methylbut-1-en-1-ol (**1**) and 2-methylbutanal (**2**); (B) and (C) NOE difference spectra resulting from irradiation of  $=\text{CCH}_3$  and  $=\text{CCH}_2$  resonances, respectively at 300 MHz (Bruker WH-300 pulsed FT spectrometer) at  $25^\circ\text{C}$  in  $\text{CD}_3\text{COCD}_3$ . Arrows indicate the shifts irradiated.

have not been made to each of **Z**- and **E**-isomer.

We are now able to distinguish one isomer from the other of **1** by the NOE difference spectra. While **Z/E**-isomers and *syn/anti*-isomers of enols were prepared from different isomers of starting materials and characterized by  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectral data,<sup>3</sup> NOE difference spectra have been rarely used to distinguish those isomers of enols.<sup>3c</sup>

Irradiation of the methyl protons ( $=\text{CCH}_3$ ) enhances the olefinic proton ( $=\text{CH}$ ) of the major isomer at  $\delta$  6.21 ppm<sup>2</sup> by 1.5% while no enhancement is observed for the olefinic proton of the minor isomer at  $\delta$  6.25 ppm<sup>2</sup> (Figure 1B). Irradiation of the methylene protons ( $=\text{CCH}_2$ ) enhances the hydroxyl proton ( $=\text{COH}$ ) by 0.5% (Figure 1C). The chemical shifts of  $-\text{OH}$  for the two isomers are so close ( $\delta$  6.52 ppm for the major isomer and  $\delta$  6.53 ppm for the minor isomer<sup>2</sup>) that it is uncertain which proton ( $\delta$  6.52 or 6.53) showed the enhancement. These NOE difference spectra strongly suggest the major isomer (*ca.* 90%) being **Z**-isomer and the minor (*ca.* 10%) being **E**-isomer. The two small negative enhancements observed for  $=\text{COH}$  in Figure 1B (with  $=\text{C}(\text{CH}_3)$  irradiation) and for  $=\text{CH}$  in Figure 1C (with  $=\text{CCH}_2$  irradiation) are also in good agreement with the structure of the **Z**-isomer. The small enhancement (0.5%) of  $-\text{OH}$  by irradiation of  $=\text{CCH}_2$  is probably because the enol **1** exists mainly in *anti*-conformation where the hydroxyl hydrogen ( $-\text{OH}$ ) is directed away from the methylene protons ( $=\text{CCH}_2$ ) and toward the olefinic proton ( $=\text{CH}$ ). This interpretation is supported by the large enhancement of  $=\text{CH}$  by irradiation of  $-\text{OH}$  (6.6%) (Figure 2) and the fact that the coupling



**Figure 2.** NOE difference spectrum in the region of  $=\text{CH}(\text{OH})$  resulting from irradiation of  $=\text{C}(\text{OH})$  resonance of 2-methylbut-1-en-1-ol (**1**) at 300 MHz (Bruker pulsed FT spectrometer) at  $25^\circ\text{C}$  in  $\text{CD}_3\text{COCD}_3$ .

constant (6.0 Hz) observed between  $=\text{CH}$  and  $=\text{COH}$  of **1**<sup>2</sup> is very close to those observed for *anti*-conformers of other enols.<sup>1b,3a</sup>

The ratio (7-9) of **Z/E**-isomer remains practically unchanged until most of **1** undergoes ketonization in  $\text{CD}_3\text{COCD}_3$ . The **Z/E**-isomer ratio seems to be determined when they are generated.

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