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# Simple Enols. 3. Stereochemistry of Simple Enols in Solution

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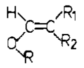
The simple enols vinyl alcohol, (*E*)-prop-1-en-1-ol, (*Z*)-prop-1-en-1-ol, and 2-methylprop-1-en-1-ol have been generated from reactive precursors in solution in slightly aqueous $CD_3COCD_3$ and their $^{1}$H NMR spectra measured under conditions where exchange of the OH proton is slow on the NMR time scale. At −80 °C $J$(OH–C$_{\alpha}$H) for vinyl alcohol and (*E*)-prop-1-en-1-ol is greater than 9 Hz whereas that for (*Z*)-prop-1-en-1-ol and 2-methylprop-1-en-1-ol is less than 6 Hz. With the former two compounds $J$(OH–C$_{\alpha}$H) decreases with temperature whereas with the latter it increases. It is concluded that the former two enols exist mainly in the *s*-cis conformation and the latter mainly in the *s*-trans conformation. The $^{13}$C NMR spectra of these enols in aqueous $CD_3COCD_3$ were also measured, and it is concluded that some factor other than a through-space shielding effect is important in determining the relative chemical shifts of the olefinic carbon atoms.

Simple enols can exist in principle in two planar conformations, *s*-cis (**1**) and *s*-trans (**2**), and a nonplanar gauche conformation (**3**). Saito interpreted the microwave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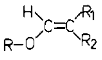
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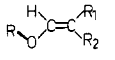
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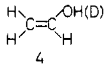
spectrum of vinyl alcohol in the gas phase in terms of the *s*-cis conformation (**1**, R = H, $R_1 = R_2$ = H),[2] and this is also the conformation favored by molecular orbital calculations. Bouma and Radom calculated the *s*-cis conformation to be 2.2 kcal mol$^{-1}$ more stable than the *s*-trans conformation and reported that "no evidence was found for a nonplanar gauche conformation".[3] Similar conformations are also possible for enol ethers. Owen and Sheppard detected by means of infrared spectroscopy two conformations of methyl vinyl ether with an enthalpy difference in the gas phase of 1.15 kcal mol$^{-1}$.[4] They considered the major "isomer" to have the *s*-cis conformation but "favored a nonplanar conformation for the second isomer". This conformation for the second "isomer" was supported by preliminary electron diffraction measurements,[5] but subsequently it was shown that the torsional angle "must be close to 180°"[6] which corresponds to the *s*-trans conformation. The *s*-cis conformation (**1**, R = $CH_3$, $R_1$ = alkyl, $R_2$ = H) was also deduced to be the major conformation for *E*-enol ethers on the basis of the effect of benzene on the $\delta$ values of the vinylic protons[7] and the long-range coupling constants between the methoxy and vinylic protons.[7] This conclusion was also supported by an analysis of their thermodynamic properties.[8] On similar grounds it was concluded that *Z*-enol ethers of aldehydes exist mainly in the *s*-trans conformation (**2**, R = alkyl, $R_1$ = H, $R_2$ = alkyl) but that those of ketones exist as a mixture of conformations including a gauche conformation.[8,9] The conformation of several more complex cyclic enol ethers has been studied by NOE difference spectroscopy, and it was concluded that "the alkyl substituent lines up cis periplanar to the region of highest bond order".[10] This usually corresponds to the *s*-cis conformation.

It should be easier to study the conformation of enols than of enol ethers since the HO–C$_{\alpha}$H coupling constants, if they could be measured, should be directly related to the dihedral angle between the HO and C$_{\alpha}$–H bonds.[11] It has recently been shown that this can be done for vinyl alcohol (**4**),[12] and we now report the measurement of these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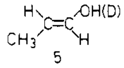
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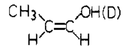
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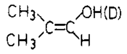
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coupling constants for three other enols (**5**–**7**) in slightly aqueous $CD_3COCD_3$ at −80 °C (Table I). It is seen that the two enols with a hydrogen cis to the hydroxyl group (**4** and **5**) have $J$(OH–C$_{\alpha}$H) > 9 Hz whereas the two enols with a methyl group cis to the hydroxyl (**6** and **7**) have $J$(OH–C$_{\alpha}$H) < 6 Hz. It is concluded that the former exist predominently in the *s*-cis conformation (**1**, R = H) and the latter in the s-trans conformation (**2**, R = H). This interpretation is supported by the long-range coupling constant $J$(OHC$_{\beta}$–*trans*-H) which for vinyl alcohol is 0.4 Hz and for (*Z*)-prop-1-en-1-ol is 0.95 Hz. If (*Z*)-prop-1-en-1-ol had the anti conformation, as proposed, the OH and the *trans*-C$_{\beta}$H would have a W relationship which is the most favorable for long-range allylic coupling[13,14] and hence should lead to a larger coupling constant.

The coupling constants $J$(OH–C$_{\alpha}$H) of all four enols vary with temperature (Figure 1).[15] Those for vinyl alcohol and (*E*)-prop-1-en-1-ol decrease with increasing temperature whereas those for (*Z*)-prop-1-en-1-ol and 2-methyl-prop-

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[1] Present address: Chemistry Department, University of Hong Kong, Pokfulam Road, Hong Kong.

[2] Saito, S. *Chem. Phys. Lett.* **1976**, *42*, 399.

[3] Bouma, W. J.; Radom, L. *J. Mol. Struct.* **1978**, *43*, 267.

[4] Owen, N. L.; Sheppard, N. *Trans. Faraday Soc.* **1964**, *60*, 634.

[5] Owen, N. L.; Seip, H. M. *Chem. Phys. Lett.* **1970**, *5*, 162.

[6] Samdal, S.; Seip, H. M. *J. Mol. Struct.* **1975**, *28*, 193. See also: Cadioli, B.; Pincelli U. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 991.

[7] Lequan, R. M.; Simonin, M.-P. *Bull. Soc. Chim. Fr.* **1970**, 4419. See also: Strobel, M. P.; Andricu, C. G.; Paquer, D.; Vazeux, M.; Pham, C. C. *Nouv. J. Chem.* **1980**, *4*, 101.

[8] Taskinen, E.; Liukas, P. *Acta Chem. Scand., Ser. B* **1974**, *28*, 114.

[9] Taskinen, E. *Tetrahedron* **1978**, *34*, 425. See also: Webb, J. G. K.; Yung, D. K. *Can. J. Chem.* **1983**, *61*, 488.

[10] Mersh, J. D.; Sanders, J. K. M. *Tetrahedron Lett.* **1981**, *22*, 4029.

[11] Cf. the dependence of coupling constant on the dihedral angle found for CH–CH bonds. Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870. Jackman, L. M.; Sternhell, S. "Applications of NMR Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon: New York, 1969; p 292.

[12] Capon, B.; Rycroft, D. S.; Watson, T. W.; Zucco, C. *J. Am. Chem. Soc.* **1981**, *103*, 1761.

[13] Barfield, M.; Spear, R. J.; Sternhell, S. *Chem. Rev.* **1976**, *76*, 593.

[14] Angular dependence of a similar long-range coupling in saturated alcohols is well established: Jochims, J. C.; Otting, W. O.; Seeliger, A.; Taigel, G. *Chem. Ber.* **1969**, *102*, 255. Kingsbury, C. A.; Egan, R. S.; Perun, T. J. *J. Org. Chem.* **1970**, *35*, 2913.

[15] In our preliminary publication (Capon, B.; Siddhanta, A. K. *Tetrahedron Lett.* **1982**, *23*, 3199) it was reported that the coupling constants for vinyl alcohol and (*E*)-prop-1-en-1-ol were, within experimental error, independent of temperature. The more accurate measurements we have now made (Brucker WP-80) show, however, that these coupling constants do in fact vary with temperature.

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Table I. Coupling Constants for Simple Enols in Aqueous $CD_3COCH_3$ at −80 °C

| enol | $\delta_{OH}$ | $J$(HO-$C_\alpha$H), Hz | $J$(HOC$_\beta$-*trans*-H), Hz | % $H_2O$ (v/v) | $10^4$[HCl], M |
|---|---|---|---|---|---|
| vinyl alcohol (**4**) | 8.46 | 9.98 | 0.40 | 0.254 | 0.254 |
| (*Z*)-prop-1-en-1-ol (**6**) | 8.07 | 5.90 | 0.95 | 0.242 | 0.968 |
| (*E*)-prop-1-en-1-ol (**5**) | 7.99 | 9.52 |  | 0.242 | 0.968 |
| 2-methylprop-1-en-1-ol (**7**) | 7.54 | 5.50 |  | 0.459 | 1.83 |

Table II. $^{13}C$ Chemical Shifts of Simple Enols and their Precursors

| compd | shift, δ $C_\alpha$ | $C_\beta$ | $C_\beta CH_3$ |
|---|---|---|---|
| vinyl alcohol (**4**)$^a$ | 149.0 | 88.0 |  |
| (*Z*)-prop-1-en-1-ol (**6**)$^b$ | 141.7 | 97.7 | 8.9 |
| (*E*)-prop-1-en-1-ol (**5**)$^b$ | 143.5 | 98.2 | 12.7 |
| dimethyl (*Z*)-prop-1-en-1-yl orthoacetate (**12**)$^{c,d}$ | 138.7 | 102.9 | 9.5 |
| dimethyl (*E*)-prop-1-en-1-yl orthoacetate (**13**)$^{c,e}$ | 139.9 | 104.1 | 12.8 |
| 2-methylprop-1-en-1-ol (**7**)$^b$ | 136.2 | 105.9 | 14.4,<br>19.8 |
| dimethyl 2-methylprop-1-en-1-yl orthoacetate (**10**)$^{c,f}$ | 133.3 | 112.4 | 15.2,<br>19.9 |

$^a$ From ref 12; −20 °C; $CD_3CN$, 10% $D_2O$ (v/v). $^b$ −10 °C; $CD_3COCD_3$, 6% $H_2O$ (v/v); $5.40 \times 10^{-4}$ M HCl. $^c$ $CDCl_3$. $^d$ δ ($OCH_3$) 49.8, δ (O-C-$CH_3$) 20.4, δ ($(RO)_3CCH_3$) 115.8. $^e$ δ ($OCH_3$) 49.8, δ (OC-$CH_3$) 202, δ ($(RO)_3CCH_3$) 115.5. $^f$ δ ($OCH_3$) 49.7, δ (OC-$CH_3$) 20.4, δ ($(RO)_3CCH_3$) 115.6.

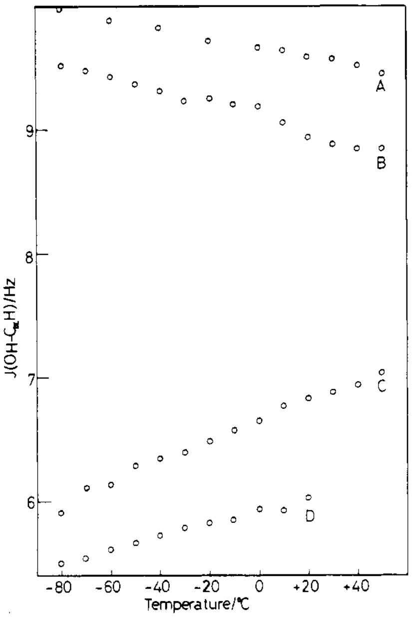


**Figure 1.** Dependence of the coupling constant $J$(OH-$C_\alpha$H) on temperature: A, vinyl alcohol; B, (*E*)-prop-1-en-1-ol; C, (*Z*)-prop-1-en-1-ol; D, 2-methylprop-1-en-1-ol. Conditions are as given in Table I.

1-en-1-ol increase. This is also consistent with the enols existing as a mixture of conformations and with the high-energy conformation being increasingly populated with increasing temperature. As the coupling constants of the pure conformations are not known, it is not possible to calculate the equilibrium constant for conformational interconversion.

Attempts have been made to correlate the $^{13}C$ chemical shifts (Table II) of the olefinic carbons of alkyl enol ethers with their conformation and with the different amounts of p–π conjugation in planar and nonplanar conformations.[16] However, Taskinen has shown that these variations in chemical shifts are best ascribed to a changing through-space shielding effect of the alkyl group (R) on the olefinic carbon atoms.[17] He showed that there was a linear correlation between the $^{13}C$-chemical shifts of the α-carbon of the *E* and *Z* isomers. The changes in $\delta_C$ with R were thought to arise from changes in the through-space shielding effect of R on the α-carbon. This was thought to be the same for both *E* and *Z* isomers as it should be independent of conformation since the distance between

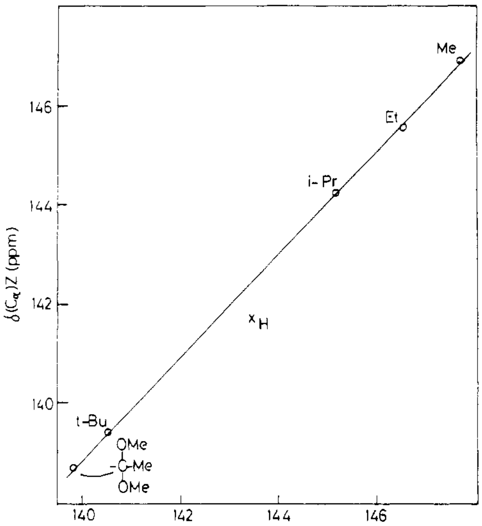
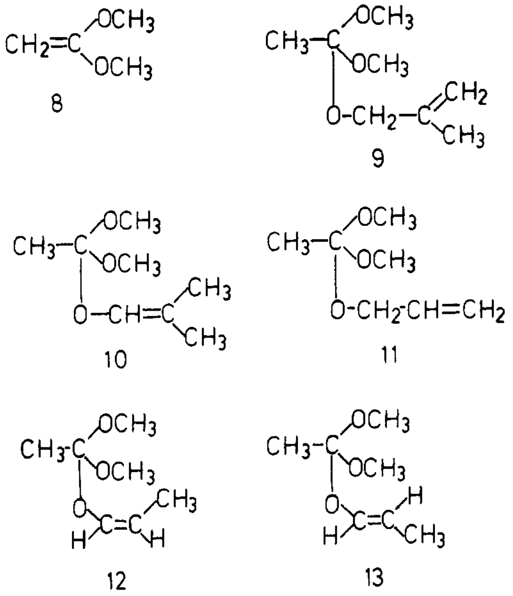


**Figure 2.** $^{13}C$ chemical shift of the α-carbon of the *Z* form of prop-1-enyl ethers (circles) and prop-1-enol (cross) against that of the *E* form.

Chart I



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(16) Hatada, K.; Nagata, K.; Yuki, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3195.

(17) Taskinen, E. *Tetrahedron* **1978**, *34*, 353.

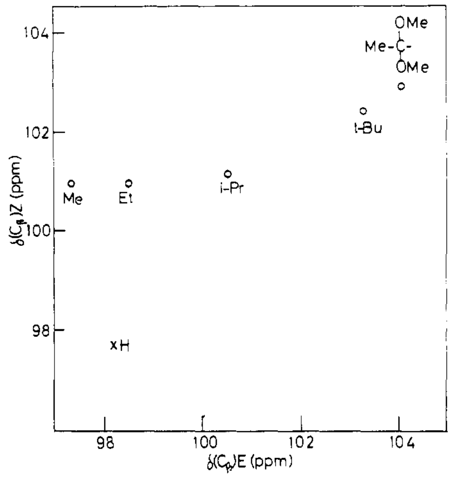

**Figure 3.** $^{13}C$ chemical shift of the $\beta$-carbon of the $Z$ form of prop-1-enyl ethers (circles) and prop-1-enol (cross) against that of the $E$ form.

R and $C_\alpha$ is the same in all of them. We are now able to add points for two more compounds to Taskinen's data. Those for the dimethyl prop-1-enyl orthoacetates (**12** and **13**, Chart I) in $CDCl_3$ lie on his lines for the propenyl ethers (Figures 2 and 3), but that for the $\beta$-carbon of the enols (**5** and **6**, measured in aqueous $CD_3COCD_3$) lies well below his line. The point for the $\alpha$-carbon of the enols does not deviate much from Taskinen's line, but it does not follow the sequence by which $\delta_C$ increases with decreasing size of R (taking R to be H). These results suggest that some effect in addition to a through-space shielding effect is important in determining the relative chemical shifts of the olefinic carbons of the prop-1-enols in aqueous $CD_3COCD_3$. The obvious difference between a hydroxyl and alkoxyl group is the ability of the former to donate a hydrogen bond to the solvent and eventually ionize. This may cause changes in the electron density and magnetic field at the olefinic carbon atoms of the enols not found with the enol ethers, so that the results for the former do not follow the correlations established with the latter.

## Experimental Section

Boiling points are uncorrected. NMR spectra were measured on Perkin-Elmer R-32 (90 MHz $^1H$) and Bruker WP80 SY (80 MHz $^1H$, 20 MHz $^{13}C$). Chemical shifts are reported in parts per million downfield from $Me_4Si$.

**Ketene Dimethyl Acetal (8).** Chloroacetaldehyde dimethyl acetal (Aldrich) was dehydrochlorinated with potassium *tert*-butoxide by using the procedure described by McElvain et al. for the preparation of ketene dimethyl acetal.[18] Ketene dimethyl acetal was distilled out of the reaction mixture along with *tert*-butyl alcohol, and the mixed distillate was used in subsequent reactions.

**Dimethyl 2-Methylprop-2-en-1-yl Orthoacetate (9).** 2-Methylprop-2-en-1-ol (Aldrich; 28.8 g, 0.4 mol) was added slowly to a solution of ketene dimethyl acetal (**8**; 28.9 g, 0.4 mol) in dry *tert*-butyl alcohol (450 mL), and an exothermic reaction took place. When the reaction appeared to be over, the *tert*-butyl alcohol was removed (rotary evaporator), and the product **9** was purified by fractional distillation: yield 50%; bp 52–54 °C (12 mm Hg); $^1H$ NMR ($CDCl_3$) $\delta$ 4.50 and 4.85 (1 H each broad signals, $=CH_2$), 3.93 (2 H, broad signal, $O-CH_2$), 3.26 (6 H, s, $OCH_3$), 1.74 (3 H, br s, $=CCH_3$), 1.44 (3 H, s, $CH_3$).

**Dimethyl 2-Methylprop-1-en-1-yl Orthoacetate (10).** This was prepared by the isomerization of **9** with KOBu-*t*/$Me_2SO$ by using the method previously reported for the conversion of allyl-protected carbohydrates into the corresponding prop-1-enyl compounds.[19] The product **10** was isolated from the reaction mixture by fractional distillation under reduced pressure: yield 60%; bp 52–54 °C (12 mmHg); $^1H$ NMR ($CDCl_3$) $\delta$ 6.03 (1 H, q of q, $J$ = 1.5, 0.5 Hz), 3.28 (6 H, s, $OCH_3$), 1.64 and 1.58 (6 H, each d with fine splitting, 1.5 and 0.5 Hz, $=C(CH_3)_2$), 1.44 (3 H, s, $CH_3$).

**Allyl Dimethyl Orthoacetate (11).** This was prepared from allyl alcohol and ketene dimethyl acetal by using a method similar to that used for the preparation of **9**: yield 40%; bp 40 °C (12 mmHg) $^1H$ NMR ($CDCl_3$) $\delta$ 5.91 (1 H, complex m, $=CH$), 5.29 (1 H, br d, $J$ = 17.2 Hz, $=CH_2$), 5.14 (1 H, br d, $J$ = 10.0 Hz, $=CH_2$), 3.97 (2 H, m, $OCH_2$), 3.25 (6 H, s, $OCH_3$), 1.42 (3 H, s, $CH_3$).

**Dimethyl ($Z$)-Prop-1-en-1-yl Orthoacetate (12).** This was prepared by isomerization of **11** with KObu-*t*/$Me_2SO$[19] and purified by fractional distillation under reduced pressure: yield 60%; bp 40 °C (12 mmHg); $^1H$ NMR ($CDCl_3$) $\delta$ 6.21 (1 H, dq, $J$ = 6.4, 1.8 Hz, $OCH=$), 4.55 (1 H, dq, $J$ = 6.4, 5.0 Hz, $=CHCH_3$), 3.23 (6 H, s, $OCH_3$), 1.63 (3 H, dd, $J$ = 5.0, 1.8 Hz, $=CHCH_3$), 1.49 (3 H, s, $CH_3$).

**Dimethyl ($Z$)- and ($E$)-Prop-1-en-1-yl Orthoacetate (12 + 13).** A 70:30 mixture of the $Z$ (**12**) and $E$ (**13**) isomers was obtained in 90% yield by the isomerization of **7** with $RuH_2(PPh_3)_4$.[20] Freshly prepared $RuH_2(PPh_3)_4$ was added to **11** in a 1:200 molar proportion, and the mixture was heated under an argon atmosphere for 1 h at 120 °C. The reaction progress was followed by $^1H$ NMR spectroscopy. The 70:30 mixture of **12** and **13** was isolated from the reaction mixture by distillation under reduced pressure: yield 90%; bp 40 °C (12 mmHg). The $^1H$ and $^{13}C$ NMR spectra indicated the presence of **12** (spectra as above) and **13**: $^1H$-NMR ($CDCl_3$) $\delta$ 6.27 (1 H, dq, $J$ = 12.2, 1.8 Hz, $OCH=$), 5.12 (1 H, q of d, $J$ = 12.2, 6.8 Hz, $CH_3CH$), 3.23 (6 H, s, $OCH_3$), 1.56 (3 H, dd, $J$ = 5.0, 1.8 Hz, $CH_3CH$), 1.47 (3 H, s, $CH_3$).

**Generation of 2-Methylprop-1-en-1-ol (7) in Solution.** This was generated from **10** in a mixture of $CD_3COCD_3$ and $D_2O$ or $H_2O$ by using a method similar to that previously described[12] for the generation of vinyl alcohol: $^1H$ NMR (−10 °C, $CD_3COCD_3$, 9% $D_2O$ (v/v), $1.27 \times 10^{-3}$ M DCl) $\delta$ 6.20 (m, $=CHOD$), 1.52 and 1.47 (2 d, $J$ = 1.15 Hz, $=C(CH_3)_2$). For the investigation of the variation of $J(OH-C_\alpha H)$ with temperature (Figure 1, Table I), **7** was generated from **10** at −10 °C in $CD_3COCD_3$–0.459% $H_2O$ (v/v) which contained $1.83 \times 10^{-4}$ M HCl.

**Generation of ($Z$)-Prop-1-en-1-ol (6) and a 70:30 Mixture of ($Z$)- and ($E$)-Prop-1-en-1-ol (6 and 5).** These were generated from **12** and from a 70:30 mixture of **12** and **13** by using a method similar to that used for the generation of vinyl alcohol: $^1H$ NMR (−10 °C, $CD_3COCD_3$, 11.2% $D_2O$ (v/v), $1.62 \times 10^{-3}$ M DCl) for ($Z$)-prop-1-en-1-ol (**6**) $\delta$ 6.32 (dq, $J$ = 6.35, 1.65 Hz, $=CHOD$), 4.15 (dq, $J$ = 6.6 Hz, $CH_3CH=$), 1.41 (dd, $J$ = 6.8, 1.7 Hz, $CH_3$); for ($E$)-prop-1-en-1-ol (**5**) $\delta$ 6.28 (dq, $J$ = 12.4, 1.5 Hz, $=CHOD$), 4.71 (dq, $J$ = 12.4, 6.5 Hz, $CH_3CH=$) 1.44 (dd, $J$ = 6.6, 1.6 Hz, $CH_3$).

For investigation of the variation of $J(OH-C_\alpha H)$ with temperature (Figure 1, Table I) **6** and **5** were generated from **12** and **13** at −10 °C in $CD_3COCD_3$–0.242% $H_2O$ (v/v) which contained $9.68 \times 10^{-5}$ M HCl.

**Generation of Vinyl Alcohol (4).** This was generated as described previously[12] from ketene methyl vinyl acetal in $CD_3COCD_3$–0.254% $H_2O$ (v/v) which contained $2.54 \times 10^{-5}$ M HCl.

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**Registry No.** **4**, 557-75-5; **5**, 57642-95-2; **6**, 57642-96-3; **7**, 56640-70-1; **8**, 922-69-0; **9**, 87938-85-0; **10**, 83661-49-8; **11**, 87938-86-1; **12**, 66178-22-1; **13**, 66178-21-0; chloroacetaldehyde dimethyl acetal, 97-97-2; allyl alcohol, 107-18-6; $RuH_2(PPh_3)_4$, 19529-00-1; ketene methyl vinyl acetal, 77302-18-2.

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(18) McElvain, S. M.; Kundiger, D. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 506.

(19) Gent, P. A.; Gigg, R.; Conant, R. *J. Chem. Soc., Perkin Trans. 1* **1972**, 248.

(20) Young, R.; Wilkinson, G. *Inorg. Synth.* **1977**, *17*, 75.