cyclopentene and bicyclo[2.1.0]pentane.

Kinetic Studies. The method used was similar to that previously reported.[4] The radical precursor was weighed into a dry, N_2 purged Pyrex tube (20 cm × 10 mm o.d.) equipped with a stirbar, sealed with a septum, and shielded from light with Al foil. The reaction tube was cooled to −78 °C, and the desired amount of trapping agent and nonane (internal standard) in THF was added. Additional THF was added to adjust the solution to a volume of 1 mL. The tube was sealed under vacuum and placed in a thermostated bath; bath temperatures were measured with a thermocouple and are believed to be accurate to within 0.5 °C. After 5 min of equilibration, the shield was removed, and the mixture was irradiated with a 150-W tungsten filament lamp at a distance of about 50 cm for 15–20 min. The tubes were cooled to −78 °C and opened, and the mixture was analyzed by GC. Ratios of low-weight hydrocarbon products were determined on the $AgNO_3$ columns; yields typically were in the range 80–100%, although lower yields were obtained in low-temperature studies with PhSeH trapping (the minimum yield was 56%). GC analyses on the DB-1 column were performed to search for high-weight products; typically, traces (<0.5%) of high-weight products were observed.

In low-temperature reactions with PhSH and PhSeH, bicyclo-[2.1.0]pentane-2-carboxylic acid (mixture of isomers) was detected by GC (DB-1) as a broad peak. For three kinetic runs performed at −78 °C, the reaction mixtures were treated with an excess of freshly prepared diazomethane, and the mixture was analyzed by GC (DB-17) to determine the ratio of *exo*- and *endo*-methyl esters.

Labeling Studies. The reactions were run in a manner similar to the kinetic studies. The reaction tube used was a 10 mm o.d. NMR tube, and the stirbar was omitted. For ArSD studies, the concentration of deuterated thiol was ca. 40 times that of PTOC **4**. For the PhSeD study, a 2-fold excess of donor was employed. The reaction mixtures contained 2–3 mg of benzene-d_6 as an internal reference. Following the reactions, the samples were analyzed by ^2H NMR spectroscopy at 29 MHz; the spectrometer was run in an unlocked mode. ^2H NMR spectra of the deuterated donors in THF showed only very minor signals in the region from δ 0 to 2.5. When referenced to internal benzene-d_6, the signal assignments for the *endo*- and *exo*-bicyclo[2.1.0]pentane-2-*d* were 0.2 ppm upfield of the literature assignments.[55] However, when referenced to external TMS, the signal assignments were *exo*-*d* δ 2.10 (lit.[55] δ 2.11) and *endo*-*d* δ 1.33 (lit.[55] δ 1.33).

For the reaction run at 1.5 °C, the low-weight hydrocarbon products (contaminated with some THF) were isolated as a mixture by preparative GC ($AgNO_3$ in ethylene glycol column). ^2H NMR spectroscopy of this mixture showed the signals for *endo*- and *exo*-bicyclo[2.1.0]pentane-2-*d* and cyclopentene-4-*d* (along with small natural abundance signals from THF) in the same ratio as found in the initial ^2H NMR analysis.

Diffusion Measurements. The method employed was the PGSE experiment described by Stejskal and Tanner[17a] based on the two-pulse spin echo sequence of Hahn[17b] and further adapted to FT techniques by James and McDonald.[17c] Measurements were performed on the Varian XL 200E spectrometer employing the dual 5-mm $^1H/^{13}C$ probe. Sample depths in the 5 mm o.d. NMR tubes were 2.5 cm. Experiments were run in nonspinning, unlocked mode with a recently described PGSE pulse sequence.[17d] ^1H spin echoes were recorded as absolute value spectra. The field gradient generated by the homospoil pulse was calibrated before each run with a sample of absolute MeOH; diffusion coefficients (D) for MeOH were those reported by Sandhu.[18a] A typical value of the field gradient was 150 mG cm^{-1}; the total variation in the field gradient over the course of the studies was about 5%. Values of D obtained for neat samples of cyclohexane, benzene, and chloroform were in good agreement with those previously reported.[18] Reasonable results were obtained over the temperature range −10 to 35 °C; at temperatures outside this range, rapid echo decay was observed presumably due to thermal gradients resulting in bulk convective mixing.

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(55) Adam, W.; Oppenlander, J. *J. Am. Chem. Soc.* **1985**, *107*, 3924.

Homogeneous Catalysis. Catalytic Production of Simple Enols

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Abstract: Complexes of the type $[Rh(diphosphine)(solvent)_2]^+$ in dry acetone or tetrahydrofuran solutions are effective catalysts for generating synthetically useful quantities of simple enols from their corresponding allylic alcohols. A representative collection of simple enols has been produced, and the physical properties and stabilities are recorded. Although these catalysts also ketonize (tautomerize) the enols to their corresponding aldehydes and ketones, the simple enols are conveniently stable in solutions containing the milder catalysts. It is found that in the absence of catalyst simple enols are remarkably stable; the enols of propanal and methyl ethyl ketone persist for up to 2 weeks in dilute acetone solutions at 25 °C. The mechanism of catalysis has been inferred from specific isotopic labeling experiments. The conclusions are as follows: the production of enols involves a hydrogen 1,3-shift mechanism involving hydrido-π-allylic intermediates; the catalytic process is essentially irreversible; and the catalytic ketonization proceeds through a hydrido-π-oxyallylic intermediate. This process is also irreversible, and the stereoselective step is the α-hydrogen abstraction from the allylic substrate. The hydrogen abstraction is probably the turnover limiting step. Three examples of chemical reactions that are unique to enols are reported and are described as proceeding by an ene mechanism.

It was long believed that enols, in the absence of kinetic steric impediments or of thermodynamic electronic stabilization, were fugacious molecules that rapidly tautomerize to the corresponding aldehydes or ketones.[1] Since enols are both acid and base sensitive[2] and possibly are even tautomerized under aprotic conditions by an intermolecular mechanism, devising suitable synthetic conditions for their production has proved elusive. It is probable that the absence of suitably mild synthetic procedures led to the supposition that enols were evanescent entities. Recent work, however, has demonstrated that simple enols can be generated and are sufficiently stable to be studied by conventional techniques. The controlled formation of these species relied on ingenious chemical[3,4] and photochemical[5-7] methods, and the relevant kinetic

(1) Hart, H. *Chem. Rev.* **1979**, *79*, 515.
(2) Toullec, J. In *Advances in Physical Organic Chemistry*; Gold, V., Bethell, D., Eds.; Academic Press: New York, 1982; Vol. 18, p 1.
(3) Ripoll, J.-L. *Nouv. J. Chim.* **1979**, *3*, 195.
(4) Capon, B.; Rycroft, D. S.; Watson, T. W.; Zucco, C. *J. Am. Chem. Soc.* **1981**, *103*, 1761. Capon, B.; Guo, B.-Z.; Kwok, F. C.; Siddhanta, A. K.; Zucco, C. *Acc. Chem. Res.* **1988**, *21*, 135 and references therein.

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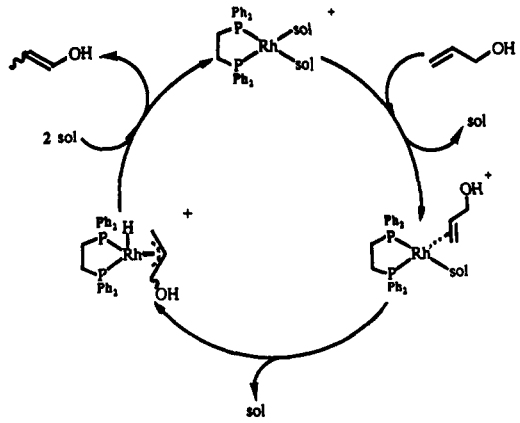
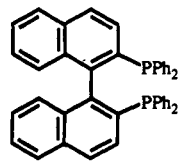


Figure 1. Illustration of the postulated mechanism of double-bond migration in the formation of enols from allylic alcohols (sol = solvent).

and thermodynamic parameters for a wide range of simple enols are now known.[7] Since the chemistry of simple enols remains largely unexplored and the current methods of generation are encumbered with a number of restrictive features, we entertained the prospect of devising a simple, mild, catalytic method for the generation of simple enols from readily available substrates. The method we describe here has its conceptual antecedents in the work on metal-catalyzed double-bond migration of allylic compounds.[8-10] Indeed, a recent report has demonstrated that metal catalysis can produce the relatively stable enol of isobutyraldehyde.[11]

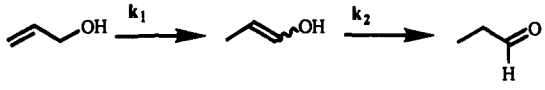
General Considerations

The cationic complex $[Rh(binap)(sol)_2]^+$, where binap = **1** and sol = weakly coordinating solvent, is an effective catalyst for double-bond migration of allylic alcohols[10] and allylic amines.[12]



1

For allylic amines, it has been established that the mechanism involves a hydrogen 1,3-shift via a π-allyl intermediate.[10] A similar mechanism probably proceeds for double-bond migration of allylic alcohols with this class of catalyst. The final product of allylic alcohol double-bond migration is the corresponding ketone or aldehyde. These were the only products observed under the conditions used (60 °C, THF, 24 h).[10] A consecutive hydrogen 1,3-shift mechanism implies, however, the intermediacy of the enol (eq 1). Given the conditioins employed, it seems unlikely that



(1)

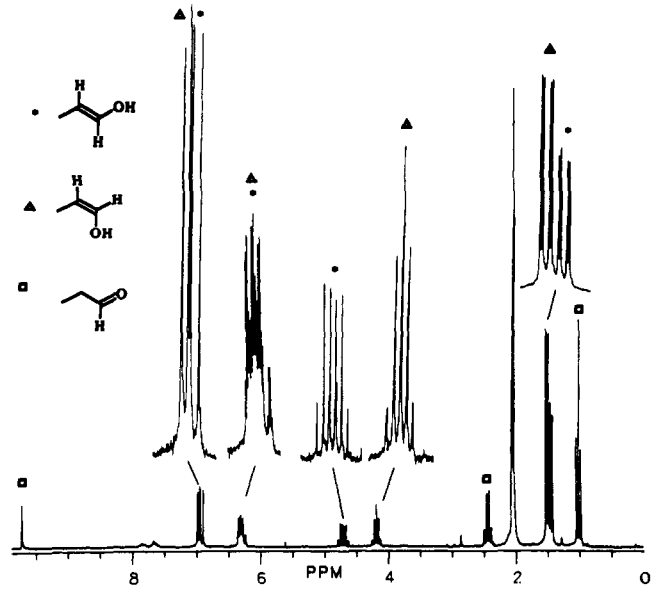
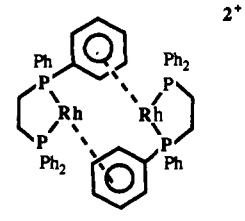


Figure 2. ^1H NMR (200-MHz) spectrum of an acetone-d_6 solution containing the two enol isomers derived from allyl alcohol, propanal, and the catalyst $[Rh(diphos)(acetone)_2]ClO_4$ at 25 °C. The starting concentration of allyl alcohol was 0.17 M, and that of the catalyst was 1.66 × 10^{-3} M. The most intense (multiplet) peak at ~2 ppm is due to residual protons of the solvent. The assignments are given in the Experimental Section.

any but the most stable enols would survive. On the other hand, were a catalytic system devised such that $k_1 \gg k_2$, the intermediate enol would accumulate.

During the course of our studies on catalytic hydroacylation[13,14] and lactonization[15] using the catalyst precursor $[Rh(diphos)]_2(ClO_4)_2$, diphos = $Ph_2PCH_2CH_2PPh_2$, and its analogues, we have found these species to be efficient catalysts for double-bond migration. The diphos catalyst exists as the arene-bridged dimer **2** in the solid state and in CH_3NO_2 and CH_2Cl_2 solutions. In dilute

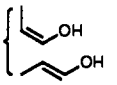
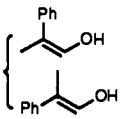
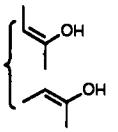
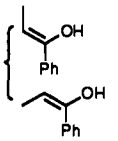
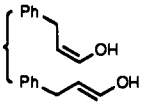
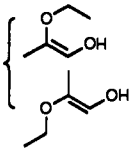
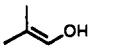
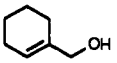
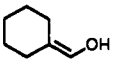


2

acetone solutions the dimer is split to form the monomer $[Rh(diphos)(acetone)_2]^+$. The coordinated acetone ligands are readily displaced by olefins.[13,14] Analogous complexes incorporating other diphosphines, $[Rh(diphosphine)(sol)_2]^+$ can be prepared in situ by controlled hydrogenation of $[Rh(diphosphine)NBD]^+$, NBD = norbornadiene. These coordinatively unsaturated complexes are ideally configured for double-bond migration via the hydrogen 1,3-shift mechanism. First, the (allylic) olefin can rapidly displace the weakly coordinated solvent molecules, and second, the necessary three coordination sites are available for accommodating the hydrido-π-allyl intermediate. These features are represented in the outline of the proposed mechanism shown in Figure 1. The basic steps involve the coordination of the olefin, followed by α-hydrogen abstraction to form the hydrido-π-allyl intermediate that upon hydride transfer to the 3-position of the π-allyl would form the enol product. Such a scheme raises the possibility that the enol itself could be converted to the aldehyde by a similar

(5) Blank, B.; Henne, A.; Laroff, G. P.; Fisher, H. *Pure Appl. Chem.* **1975**, *41*, 475.
(6) Haag, R.; Wirz, J.; Wagner, P. J. *Helv. Chim. Acta* **1977**, *60*, 2595.
(7) Kresge, A. J. *CHEMTECH* **1986**, 250 and references cited therein. Keeffe, J. R.; Kresge, A. J.; Schepp, N. P. *J. Am. Chem. Soc.* **1988**, *110*, 1993. Kresge, A. J. *Acc. Chem. Res.* **1990**, *23*, 43. Keeffe, J. R.; Kresge, A. J.; Schepp, N. P. *J. Am. Chem. Soc.* **1990**, *112*, 4862.
(8) Bottechi, C.; Giacomelli, G. *Gazz. Chim. Ital.* **1976**, *106*, 1131.
(9) Sasson, Y.; Rempel, G. L. *Tetrahedron Lett.* **1974**, 4133.
(10) Tani, K. *Pure. Appl. Chem.* **1985**, *57*, 1845 and references cited therein.
(11) Park, J.; Chin, C. S. *J. Chem. Soc., Chem. Commun.* **1987**, 1213. Chin, C. S.; Lee, S. Y.; Park, J.; Kim, S. *J. Am. Chem. Soc.* **1988**, *110*, 8244.
(12) Tani, K.; Yamagata, T.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H.; Miyashita, A.; Noyori, R.; Otsuka, S. *J. Am. Chem. Soc.* **1984**, *106*, 5208.
(13) Fairlie, D. P.; Bosnich, B. *Organometallics* **1988**, *7*, 936.
(14) Fairlie, D. P.; Bosnich, B. *Organometallics* **1988**, *7*, 946.
(15) Bergens, S. H.; Fairlie, D. P.; Bosnich, B. *Organometallics* **1990**, *9*, 566.

Table I. Catalytic Production of Enols[a]

entry	substrate	time[b]	% enol	isomer ratio[e]	% keto
1		14 min	89	 1 (1) 1.1 (1.2)	11
2		330 min	86	 1 (2.2) 1 (1)	14[c]
3		9 min	83	 5.3 (3.6) 1 (1)	18
4		124 min	47	 all (11) 0 (1)	53
5		167 min	48	 1 (1.7) 1.7 (1)	45[d]
6		50 h	42	 0 (0) all (all)	polymer
7		16 min	96		4
8		27 h	71		29

[a] Catalyst = $[Rh(diphos)]^+$; catalyst concentration = 1.66×10^{-3} M [Rh]; solvent = acetone; temperature = 25 °C; substrate concentration = 0.17 M; ratio of substrate to catalyst = 100:1. [b] Time required to convert ~98% of the allylic alcohol. [c] Catalyst = $[Rh(binap)]^+$; catalyst concentration = 2.87×10^{-3} M; substrate concentration = 1.33×10^{-1} M; ratio of substrate to catalyst = 46:1. [d] Same conditions as *c* except solvent = THF. [e] Initial (kinetic) ratio shown in parentheses—unenclosed ratio at ~98% consumption of allylic alcohol.

catalytic mechanism involving a π-oxyallyl intermediate.

Enol Production

When allyl alcohol (0.17 M) in dry, freshly distilled acetone is allowed to react with the catalyst $[Rh(diphos)]_2(ClO_4)_2$ (1.66×10^{-3} M in Rh; 1M % [Rh]) at 25 °C, the allyl alcohol is completely consumed after 15 min to give ~90% of the corresponding *Z*- and *E*-enols in approximately equal proportions. The remaining product is propionaldehyde. No other species were detected. When this solution is allowed to stand at 25 °C, both enols slowly ketonize (tautomerize) to the aldehyde. Figure 2 shows the ^1H NMR (200-MHz) spectrum of the catalytic acetone-d_6 solution ~20 min after catalysis began. The peak assignments are discussed in the Experimental Section. Addition of ~5% D_2O to the solution of enols leads to immediate exchange of the alcohol proton of the enol but does not perceptibly accelerate ketonization. On the other hand, addition of a catalytic amount of *p*-toluenesulfonic acid to the dry acetone solution of the enols causes instantaneous ketonization.

Figure 3 shows plots of the concentrations of various species at different times during the catalysis under the catalytic conditions just described. We observe that the *E*-enol is produced and dissipated faster than the *Z*-enol under these conditions. Both enols, however, are conveniently stable at 25 °C.

Table I lists a number of allylic alcohols that were converted to the corresponding enols. The $[Rh(diphos)]^+$ catalyst in acetone solutions was mostly used, although we found that $[Rh(binap)]^+$ was more efficient in two of the cases, one of which was performed in THF. We present the data in terms of the amount of enol present after all of the allylic alcohol has been consumed. Two

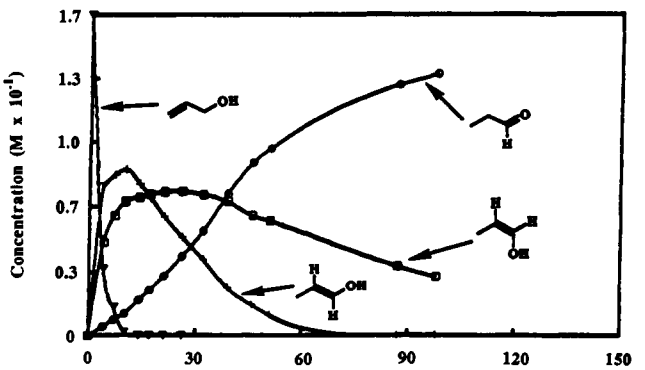
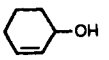
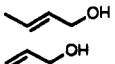
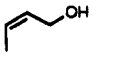


Figure 3. Concentration versus time plot of the various species in solution for the production of enols from allyl alcohol using the 1M % $[Rh(diphos)]^+$ catalyst in acetone-d_6 solution at 25 °C.

ratios for the *Z*- and *E*-enols are provided, one when all of the allylic alcohol has been consumed and the other for the initial ratio of isomers. The divergence in these ratios arises from the fact that the *Z*- and *E*-enol isomers have different rates of ketonization under the catalytic conditions. Since, as we show presently, the catalyst does not cause perceptible equilibration of the enol isomers, the initial enol isomer ratios given in Table I represent kinetic ratios.

Inspection of Table I reveals that catalysis is remarkably clean; only the enols and their keto forms are present, except for entry

Table II. Catalytic Production of Enols[a]

entry	substrate	time[c] (h)	% enol	% keto	time[d] (min)	max % enol	% substrate
9		3	0	100	26	24	54
10[b]		8	0	100	23	39[e]	23
11[b]		7	0	100	42	32[e]	42

[a] For entry 9: catalyst = $[Rh(diphos)]^+$; catalyst concentration = 1.66×10^{-3} M [Rh]; solvent = acetone; temperature = 25 °C; substrate concentration = 0.17 M; ratio of substrate to catalyst = 100:1. [b] Same as in *a* except substrate concentration = 0.34 M; ratio of substrate to catalyst = 200:1. [c] Time required to convert ~98% of the allylic alcohol. [d] Time required to produce the maximum amount of enol. [e] The ratio of isomers is discussed in the text.

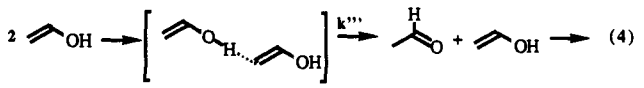
6 where slow polymerization occurs. Allylic alcohols bearing phenyl groups are generally transformed more slowly as evidenced by a comparison of entries 2 and 7 and of 3 and 4. This catalytic retardation in rate is probably due, at least in part, to π-aryl binding to the catalyst, a phenomenon that has been demonstrated previously with these catalysts.[16] Given the mechanism of catalysis, which we infer presently, the π-aryl binding mode is likely to be catalytically unproductive, serving only to tie up the catalyst. Entry 8 also represents a slowly converted precursor, and we ascribe its sluggishness to steric factors. Finally, it will be noted that catalysis can produce one enol isomer exclusively or in nearly equal proportions depending on the nature of the substrate. We discuss the origins of this stereoselectivity later.

Although the substrates in Table I produce substantial concentrations of enols after all of the substrates have been consumed, we have encountered other substrates for which no enol is present at this stage. In these cases, however, practical amounts of the enols are produced before all of the substrate is consumed. Table II lists three substrates of this type and includes the time for complete conversion of the substrate and the maximum amount of enol produced during catalysis. It is clear that in these cases the rates of enol production compared to the rates of ketonization are not sufficiently different to obtain the enols free of the substrate. If the presence of the allylic alcohol can be tolerated, however, practical quantities of these enols are obtained.

The results in Tables I and II generally refer to 1.66×10^{-3} M [Rh] and 0.17 M substrate concentrations (100:1 substrate to catalyst ratio). This choice was not accidental, since we found these conditions to be optimal for the production of enols with most of the substrates. We assume the amount of enol that can be produced under antiseptic conditions is dependent on the interplay of the following rates and equilibria. On the basis of these assumptions, the rate of enol formation should increase with an increase in concentration until all of the catalyst is bound as the catalytically productive adduct, [Sub·Cat], eq 2. A similar effect should be observed for catalytic ketonization, eq 3. The rate of the intermolecular thermal ketonization path, eq 4, should also increase with increase in concentration.

$$\text{Cat} + \text{Sub} \rightleftharpoons [\text{Cat·Sub}] \xrightarrow[-\text{Cat}]{k'} \text{Enol} \qquad (2)$$

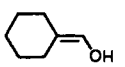
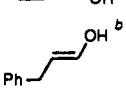
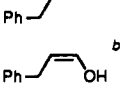
$$\text{Cat} + \text{Enol} \rightleftharpoons [\text{Cat·Enol}] \xrightarrow[-\text{Cat}]{k''} \text{keto form} \qquad (3)$$



(4)

With these considerations in mind, we investigated a number of substrates at higher concentrations but the original concentration of catalyst, 1.66×10^{-3} M [Rh], was retained. Using 1000 equiv (1.7 M) of 2-methylpropenol (entry 7) in acetone at 25 °C and the $[Rh(diphos)]^+$ catalyst, we find that, first, the turnover frequency is much faster than under the conditions specified in Table I and, second, only pure enol is present when all of the substrate is consumed. Thus, in this case the higher substrate concentration leads to a more efficient production of the enol. We note, however, that the enol of isobutyraldehyde is especially stable. Under the same conditions, allyl alcohol (entry 1) catalysis behaves in an unexpected way. At these higher concentrations, the catalysis proceeds more quickly, as expected, but when the total enol concentration reaches ~0.6 M, there is sudden catastrophic ketonization. Almost complete ketonization occurs over 3 min when the critical concentration is reached. We have been unable to determine the cause of the sudden onset of ketonization but, as a practical matter, we observe that up to ~0.5 M enol concentrations are stable. Also investigated were the allylic alcohols shown in entries 3 and 9–11 at 1000:1 substrate to catalyst ratios. In all of these cases, the catalytic rate increased but the rate of ketonization increased even more, so that less enol was produced than under the conditions specified in Tables I and II. We conclude that the conditions specified in Tables I and II are probably close to optimal for most substrates.

Table III. Time Required To Ketonize ~98% of the Enol in Acetone-d_6 Solutions Containing the Catalyst $[Rh(diphos)]^+$[a]

enol	init conc (M)	time
	0.075	120 min
	0.083	40 min
	0.17	8 days
	0.122	180 min
	0.023	50 min
	0.083	5.5 h
	0.13	5 days
 [b]	0.024	~6 h
 [b]	0.040	~8 h

[a] Catalyst concentration = 1.66×10^{-3} M, 25 °C. [b] Catalyst = $[Rh(binap)]^+$; catalyst concentration = 2.87×10^{-3} M; THF.

Kinetic Enol Stabilities

The kinetic stabilities of the various enols, expressed in terms of the initial concentration and the time taken for ~98% ketonization at 25 °C, are listed in Table III under the conditions specified. The stabilities correlate reasonably with steric and electronic factors except that *E*-enol isomers appear to be less stable than the *Z* isomers under these conditions.

Implicit in eqs 3 and 4 is the expectation that if the catalytic ketonization path were suppressed, the lives of the enols would be extended. We have attempted to deactivate the catalyst to

(16) Halpern, J.; Riley, D. P.; Chan, A. S. C.; Pluth, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 8055.

Table IV. Time Required for ~98% Conversion of Allyl Alcohol by the Catalysts [Rh(diphosphine)]$^+$ in Acetone Solutions at 25 °C and the Proportion of Products at This Time[a]

diphosphine	time (min)	% enol	cis:trans	% keto
$Ph_2P(CH_2)_2PPh_2$(diphos)	14	89	0.9:1	11
$Cy_2P(CH_2)_2PCy_2$(cyphos)	<5	0		100
$Ph_2P(CH_2)_3PPh_2$(dppp)	45	0		100[b]
$Ph_2P(CH_2)_4PPh_2$(dppb)	19	25	0.9:1	75
BINAP	21	80.4	1.2:1	19.6

[a] Concentration of allyl alcohol = 0.28 M; concentration of catalyst = 2.88×10^{-3} M. [b] Maximum enol after 9 min; 16% enol (cis:trans = 0.8:1), 47% keto, 37% allyl alcohol.

ketonization in a number of ways, none of which were completely successful. Thus, addition of 6 equiv of CH_3CN or 1 equiv of diphos to give the presumably catalytically inactive species, $[Rh(diphos)(CH_3CN)_2]^+$ and $[Rh(diphos)_2]^+$, respectively, led to rapid ketonization. The origins of this accelerated ketonization are not understood by us. Addition of 1 equiv of dimethyl fumarate suppressed ketonization slightly. Only the addition of CO to form $[Rh(diphos)(CO)_2]^+$ significantly enhanced the enol stability, in some cases by a factor of 10. Even so, CO binding was not completely successful in suppressing ketonization catalysis, possibly because of CO dissociation. One remaining option was to remove the enol from the catalyst.

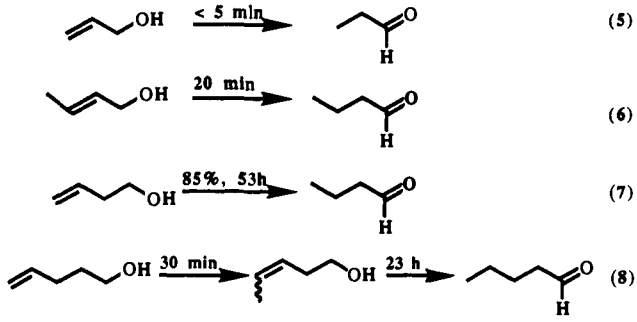
Enols derived from the allylic alcohols listed as entries 1 and 3 were separated from the catalyst by low-temperature bulb to bulb transfer at the stage when all of the allylic alcohols were consumed. This manipulation, however, led to considerable ketonization, giving an acetone solution of *E*- and *Z*-enols derived from allyl alcohol in a ratio of 1:9 (*E*/*Z*) and a total concentration of 0.03 M. Only the *Z*-enol for entry 3 was obtained by this method in a concentration of 0.014 M. The rest of the materials were the corresponding keto forms. The starting concentration of both allylic alcohol substrates was 0.17 M. The enol solutions are very stable under these conditions. We find that the enols of propanol (entry 1) take about 15 days to completely dissipate. The *Z* and *E* isomers convert at roughly the same rate. Perhaps surprisingly, the *Z*-enol of methyl ethyl ketone (entry 3) is nearly as stable; it takes about 14 days to ketonize completely. A comparison of enol stability in the presence and absence of catalyst indicates that essentially all of the ketonization that occurs in solutions containing catalyst (Table III) is due to catalytic ketonization and not due to a thermal path. The intrinsic enol stability is remarkable and significant for it suggests that under proper conditions simple enols are much more stable than hitherto supposed. Further, enols derived from ketones are nearly as stable as those derived from aldehydes despite the greater thermodynamic driving force of the former.[7] Although we have taken great care to achieve antiseptic conditions, we remain unpersuaded that the ketonization that occurs in pure acetone is due to an intermolecular path such as that depicted in eq 4. Ketonization might be caused by the glass surface or by minute amounts of adventitious impurities. Despite their now found stabilities, enols are sensitive molecules.

Catalyst Variation

Because the successful generation of enols depends on a delicate balance of factors, we investigated a number of related catalysts. Table IV lists the results with catalysts of the type [Rh(diphosphine)]$^+$ using allyl alcohol as the substrate. These results suggest that the diphos and binap catalysts are the most effective, that increasing the aliphatic chelate ring diminishes the efficiency, and that the [Rh(cyphos)]$^+$, cyphos = $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$, catalyst is the most powerful double-bond migration catalyst. Using 1M % [Rh(cyphos)]$^+$ in acetone at 25 °C, allyl alcohol is converted to the aldehyde essentially upon mixing.

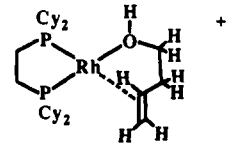
Homoallylic Substrates

In addition to allylic alcohol substrates, we have investigated homoallylic alcohols as precursors to enols. Using the [Rh(diphos)]$^+$ catalyst, we find that unlike allyl alcohol, which is rapidly converted, homoallyl alcohol is almost inert the the catalyst. In order to assess the origins of this catalytic inhibition, we compared the catalytic rates of a number of substrates with the more active catalyst [Rh(cyphos)]$^+$. The results are summarized in eqs 5–8.



In no case was any enol detected during catalysis. We observe that steric hinderance slows the catalysis (eqs 5 and 6) but that a special factor operates in slowly catalysis for homoallylic alcohols (eq 7). Consistently, when the aliphatic chain is extended further (eq 8), the first double-bond migration proceeds at a "normal" rate but catalysis gets "stuck" at the homoallylic stage. The most obvious explanation for the homoallylic inhibition is that a stable catalyst–substrate adduct is formed either that is catalytically inactive or that is converted much more slowly than other adducts. We believe we have structurally defined the catalytically unproductive adduct in the following way.

The catalyst [Rh(cyphos)(acetone)$_2$]$^+$ was combined with approximately 1 equiv of homoallyl alcohol in acetone at 30 °C. The ^{1}H NMR of the stable species formed is consistent with the stable five-membered chelate ring structure **3**. Thus, all of the homoallyl



3

alcohol protons of **3** have chemical shifts different from those of the free ligand, and moreover, the vinylic protons show rhodium coupling. The details are given in the Experimental Section. It appears, therefore, that homoallylic alcohols form stable chelate structures with the [Rh(diphosphine)]$^+$ species and that this type of binding is catalytically unproductive for double-bond migration because the rhodium atom is sterically constrained from interacting with the requisite hydrogen atoms.

Mechanistic Questions

Although we have alluded to some of the mechanistic features of catalytic enol formation, we now address certain specific questions. First, is it possible to intercept any of the putative catalytic intermediates? Second, what is the mechanism of a catalytic conversion of allylic alcohols to their enols? Third, is this conversion a reversible process under the present conditions? Fourth, what is the catalytic mechanism for the ketonization of enols? Fifth, at what step in the catalytic cycle is the *Z*- and *E*-enol selectivity determined?

The Black Box

We have attempted to intercept catalytic intermediates by following the catalysis at low temperature by ^{1}H NMR using acetone solutions and 4 equiv of allyl alcohol with [Rh(diphos)]$^+$. No reaction was observed at temperatures below 0 °C. At 0 °C, catalysis began but no species other than the catalyst, substrate, and product were detected. We found, using the [Rh(cyphos)]$^+$ catalyst under similar conditions, that catalysis of allyl alcohol occurred rapidly at −80 °C, attesting to the potency of the cyphos catalyst. It thus appears that catalytic production of enols by these catalysts is another example of "black box" catalysis where, as it were, the substrate and catalyst enter the black box in which the substrate is transformed to emerge as the product. The nature of the catalytic intermediates was inferred from specific isotopic

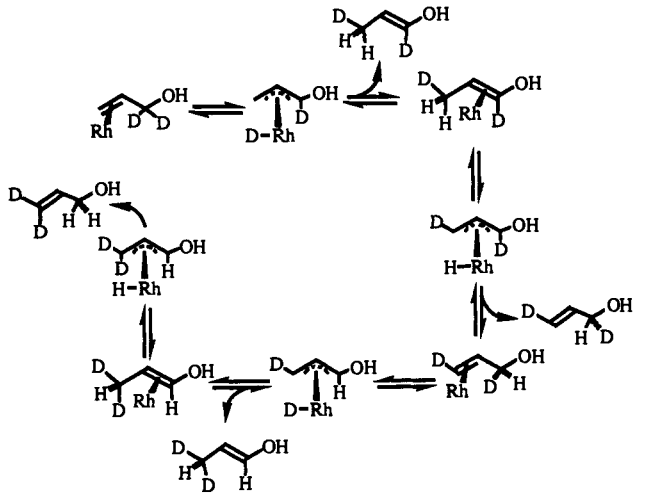
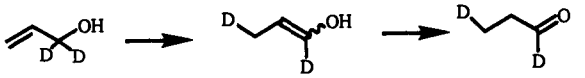


Figure 4. Illustration of a possible mechanism that could scramble the deuterium atoms of the allyl alcohol **4** if the catalytic process were reversible. The stereochemistries of some of the π-allylic intermediates are not completely specified for simplicity of presentation. No scrambling is observed.

labeling, the implications of which are embodied in the mechanism postulated in Figure 1.

Enol Production Mechanism and Reversibility

The π-allylic mechanism requires that a hydrogen 1,3-shift mechanism operates so that the specifically labeled substrate **4** should produce the specifically labeled products **5** and **6**. By use

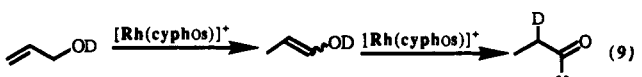


4 **5** **6**

of the diphos catalyst and substrate **4**, the only products observed by ^2H and ^1H NMR were the specifically labeled products **5** and **6** with a single deuterium atom at each of the 1- and 3-positions. This result is consistent with the existence of the postulated hydrido-π-allylic intermediate (Figure 1). Furthermore, the equal deuterium distribution between the 1- and 3-positions implies that the two major steps in the mechanism, the hydrido-π-allyl formation and the hydrido transfer to the 3-position, are irreversible. Were both these steps reversible, we would expect to observe unequal distribution of the labels between the 1- and 3-positions and the appearance of scrambling of the label in the substrate during catalysis. Neither is observed. The reversible mechanism that could give rise to (the unobserved) scrambling is illustrated in Figure 4. It is possible, however, that either of the steps be irreversible and the other reversible and still get the same result. Since both steps involve the common hydrido-π-allylic intermediate, such cases seem improbable.

Catalytic Ketonization Mechanism

There are a number of mechanisms that can be postulated for the catalytic ketonization of enols, but the simplest is a mechanism analogous to the one illustrated for the catalytic production of enols from allylic alcohols (Figure 1). The postulated mechanism is shown in Figure 5, where an oxyallyl intermediate is invoked. We have used the cyphos catalyst and the deuterated substrate **7** to determine whether the postulated deuterium 1,3-shift occurs (eq 9). The cyphos catalyst was chosen because it is certain that



7 **8** **9** (9)

all of the ketonization that occurs is due to the catalyst. We find by ^2H and ^1H NMR that the deuterium is transferred exclusively to the position shown in **9**. Although in the aprotic conditions used, a thermal ketonization path would also place the deuterium in the position shown in **9**, the fact that catalytic ketonization does

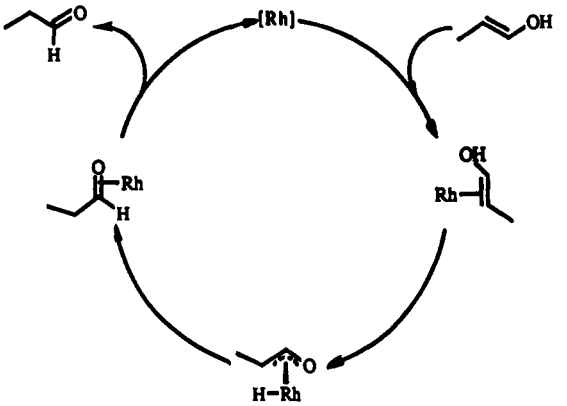
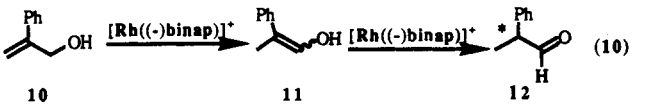


Figure 5. Illustration of the proposed π-oxyallyl mechanism for catalytic ketonization of enols.

not lead to deuterium scrambling among the other positions of **9** suggests that the simple mechanism outlined in Figure 5 obtains. Further, the oxyallyl mechanism implies that the substrate and catalyst are intimately associated and suggests that a chiral catalyst should be enantioselective if a prochiral substrate were used. When the optically active catalyst $[Rh((-)binap)]^+$ is employed, the prochiral substrate **10** is transformed to the chiral aldehyde **12** in 18% ee (eq 10). Since the enantioselective step in this process



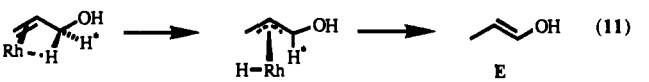
10 **11** **12** (10)

is the conversion of **11** to **12**, it is clear that ketonization is not proceeding completely by a thermal bath and that the mechanism of catalytic ketonization probably involves intimate association of the enol **11** with the catalyst.

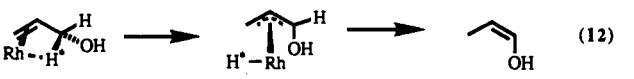
Under similar conditions, we find with the diphos catalyst that enol production, **4** to **5**, and the catalyzed ketonization, **8** to **9**, are considerably slower with the deuterated substrates, **4** and **8**. As a consequence, the isotope effect retards ketonization, giving greater proportions of enols during catalysis. For example, we find that 30 min after the undeuterated and O-deuterated allyl alcohols were consumed there remained ~50% of the undeuterated enol and ~88% of the O-deuterated enol. This isotope effect may prove to be an effective method of increasing the enol concentration with other substrates. The isotope effects imply that the catalytic turnover limiting step involves either the hydrogen-abstraction or the hydrogen-transfer step. We suspect that the initial hydrogen abstraction is the turnover limiting step.

Stereoselective Step

There are two possible steps in the catalytic cycle where the stereoselection could occur. These are illustrated in eqs 11 and 12. Abstraction of the unlabeled hydrogen atom in eq 11 gives



E (11)



Z (12)

a hydrido-π-allyl intermediate where the hydroxyl group is syn disposed. Transfer of the hydrido ligand to this π-allyl structure leads to the *E*-enol. Abstraction of the other (labeled) hydrogen atom requires rotation about the carbon–carbon single bond and gives the π-allyl with an anti-disposed hydroxyl group. Hydrido transfer to this π-allyl structure gives the *Z*-enol (eq 12). Were these the only mechanistic occurrences, the kinetic proportions of *E*- and *Z*-enols would depend only on the relative rates at which the two (stereogenic) hydrogen atoms were abstracted. There is the possibility, however, that the two π-allyl intermediates could interconvert (syn $\rightleftharpoons$ anti) by the π–σ–π mechanism.[17] If the

Table V. ^1H and ^2H NMR Data of Enols and Reaction Products

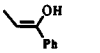
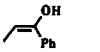
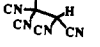
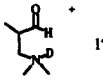
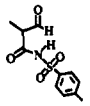
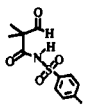
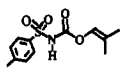
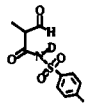
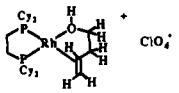
compd	NMR data
	^1H NMR (500 MHz, $(CD_3)_2CO$) δ 6.95 (d, J = 8.8 Hz, 1 H, O*H*), 6.30 (ddq, J = 12.3, 9.0, 1.5 Hz, 1 H, C=C*H*O), 4.72 (dq, J = 12.5, 6.6 Hz, 1 H, MeC*H*=C), 1.45 (dd, J = 6.6, 1.8 Hz, 3 H, CH_3)[28]
	^1H NMR (300 MHz, $(CD_3)_2CO$) δ 6.98 (dd, J = 6.8, 0.7 Hz, 1 H, O*H*), 6.29 (m, 1 H, C=C*H*O), 4.18 (ddq, J = 6.6, 0.7, 6.8 Hz, 1 H, MeC*H*=C), 1.50 (dd, J = 6.8, 1.7 Hz, CH_3)[28]
	^1H NMR (200 MHz, $(CD_3)_2CO$) δ 6.47 (d, J = 6.2 Hz, 1 H, O*H*), 6.18 (dt, J = 6.1, 0.3 Hz, 1 H, C=C*H*O), 2.05–1.28 (m, 10 H)[29]
	^1H NMR (200 MHz, $(CD_3)_2CO$) δ 6.45 (d, J = 6.0 Hz, 1 H, O*H*), 6.18 (d*, J = 6 Hz, 1 H, C=C*H*O), 1.54 (s, 3 H, CH_3), 1.47 (s, 3 H, CH_3)[11a]
	^1H NMR (300 MHz, $(CD_3)_2CO$) δ 6.81 (s, 1 H, O*H*), 4.45 (q, J = 6.8 Hz, 1 H, MeC*H*=C), 1.67 (s, 3 H, C=C(CH_3)O), 1.45 (d, J = 6.4 Hz, 3 H, CH_3C(H)=C)[30]
	^1H NMR (300 MHz, $(CD_3)_2CO$) δ 6.61 (s, 1 H, O*H*), 4.05 (q, J = 6.6 Hz, 1 H, (Me)C*H*=C), 1.72 (s, 3 H, C=C(CH_3)O), 1.47 (d*, J = 6.6 Hz, 3 H, CH_3C(H)=C)[30a]
	^1H NMR (300 MHz, $(CD_3)_2CO$) δ 6.90 (s, 1 H, O*H*), 4.65 (t, J = 4.0 Hz, 1 H, C*H*=C), 2.04–1.41 (m, 8 H)[31]
	^1H NMR (300 MHz, $(CD_3)_2CO$) δ 6.01 (d, J = 11.1 Hz, 1 H, O*H*), 5.70 (dq, J = 11.0, 1.2 Hz, 1 H, C=C*H*O), 3.76 (q, J = 7.0 Hz, 2 H, OCH_2Me), 1.61 (d, J = 1.2 Hz, 3 H, (EtO)CH_3C=C), 1.17 (t, J = 7.0 Hz, 3 H, OCH_2CH_3)
	^1H NMR (300 MHz, $(CD_3)_2CO$) δ 7.90–7.05 (m, 6 H, Ph and O*H*), 6.69 (dq, J = 5.9, 1.2 Hz, 1 H, C=C*H*O), 1.85 (d, J = 1.3 Hz, 3 H, CH_3)[32]
	^1H NMR (300 MHz, $(CD_3)_2CO$) δ 7.90–7.05 (m, 6 H, Ph and O*H*), 7.01 (dq, J = 6.0, 1.3 Hz, 1 H, C=C*H*O), 1.96 (d, J = 1.3 Hz, 3 H, CH_3)[32]
	^1H NMR (500 MHz, $(CD_3)_2CO$) δ 6.89 (d, J = 6.8 Hz, 1 H, O*H*), 6.3–6.2 (m, 1 H, C=C*H*O), 4.15 (dt, J = 7.0, 6.8 Hz, 1 H, EtC*H*=C), 2.05 (m, 2 H, CH_2Me), 0.92 (m, CH_3, obscured)[33]
	^1H NMR (500 MHz, $(CD_3)_2CO$) δ 6.85 (d, J = 9.3 Hz, 1 H, O*H*), 6.3–6.2 (m, 1 H, C=C*H*O), 4.76 (dt, J = 11.6, 7.3 Hz, 1 H, MeC*H*=C), 1.85 (dq, J = 7.34, 7.34 Hz, MeCH_2), 0.92 (m, CH_3, obscured)[33]
	^1H NMR (300 MHz, $(CD_3)_2CO$) δ 6.93 (s*, 1 H, O*H*), 4.68 (t*, J = 6.8 Hz, 1 H, CH_2DCH=C), 1.42 (dt, J = 6.6, 2.2 Hz, 2 H, CH_2D)[28a] $^2H\{^1H\}$ NMR (46 MHz, $(CH_3)_2CO$) δ 6.34 (s, 1 D, C=C*D*OH), 1.51 (s, 1 D, CH_2D)
	^1H NMR (300 MHz, $(CD_3)_2CO$) δ 6.98 (s, 1 H, O*H*), 4.17 (t, J = 6.5 Hz, 1 H, CDH_2CH=C), 1.49 (dt, J = 6.7, 2.2 Hz, 2 H, CH_2D)[28] $^2H\{^1H\}$ NMR (46 MHz, $(CH_3)_2CO$) δ 6.34 (s, 1 D, C=C*D*OH), 1.51 (s, 1 D, CH_2D)
	^1H NMR (500 MHz, $(CD_3)_2CO$) δ 2.42 (t*, J = 7.4 Hz, 2 H, CH_2DCH_2), 1.00 (dt, J = 7.4, 2.0 Hz, 2 H, CH_2D)[a] $^2H\{^1H\}$ NMR (46 MHz, $(CH_3)_2CO$) δ 9.76 (s, 1 D, C*D*O), 1.01 (s, 1 D, CH_2D)
	^1H NMR (300 MHz, $(CD_3)_2CO$) δ 6.32–6.25 (m, 1 H, C=C*H*OD), 4.18 (dq, J = 6.6, 6.8 Hz, 1 H, MeC*H*=C), 1.51 (dd, J = 6.7, 1.7 Hz, 3 H, CH_3)[28]
	^1H NMR (300 MHz, $(CD_3)_2CO$) δ 6.32–6.25 (m, 1 H, C=C*H*OD), 4.70 (dq, J = 12.3, 6.6 Hz, 1 H, MeC*H*=C), 1.44 (dd, J = 6.7, 1.7 Hz, 3 H, CH_3)[28]
	^1H NMR (300 MHz, $(CD_3)_2CO$) δ 9.74 (s, 1 H, C*H*O), 2.43 (m, 1 H, MeC*H*D), 1.00 (dt, J = 7.3, 1.2 Hz, 3 H, CH_3) $^2H\{^1H\}$ NMR (61 MHz, $CH_3)_2CO$) δ 2.34 (s, MeCH*D*)
	^1H NMR (300 MHz, THF-d_8) δ 7.7–7.0 (m, 6 H, Ph and O*H*), 6.41–6.31 (m, 1 H, C=C*H*O), 4.33 (dt, J = 6.7, 7.1 Hz, 1 H, $PhCH_2CH$=C), 3.39 (dd, J = 7.4, 0.9 Hz, 2 H, $PhCH_2$)[34]
	^1H NMR (300 MHz, THF-d_8) δ 7.7–7.0 (m, 6 H, Ph and O*H*), 6.41–6.31 (m, 1 H, C=C*H*O), 4.81 (dt, J = 12.2, 7.4 Hz, 1 H, $PhCH_2CH$=C), 3.17 (*d*, J = 7.4 Hz, 2 H, $PhCH_2$)[34]
	^1H NMR (300 MHz, $(CD_3)_2CO$) δ 7.6–7.2 (m, 5 H, Ph), 7.15 (s, 1 H, O*H*), 5.06 (q, J = 7.2 Hz, 1 H, MeC*H*=C), 1.74 (d, J = 7.0 Hz, 3 H, CH_3)[35]
	^1H NMR (300 MHz, $(CD_3)_2CO$) δ 7.6–7.2 (m, 6 H, Ph and O*H*), 1.62 (d, J = 7.2 Hz, 3 H, CH_3),[35] (MeC*H*=C), obscured)
	^1H NMR (500 MHz, THF-d_8) δ 9.48 (s, 1 H, C*H*O), 5.87 (s, 1 H, $(CN)_2CH$), 3.69 (q, J = 7.4 Hz, 1 H, C*H*(Me)), 1.63 (d, J = 7.5 Hz, 3 H, CH_3)
	^1H NMR (300 MHz, THF-d_8) δ 9.40 (s, 1 H, C*H*O), 5.74 (s, 1 H, $(CN)_2CH$), 1.59 (s, 6 H, $C(CH_3)_2$)
	^1H NMR (200 MHz, THF-d_8) δ 9.50 (s, 1 H, C*H*O), 3.69 (q, J = 7.4 Hz, 1 H, C*H*(Me)), 1.62 (d, J = 7.4 Hz, 3 H, CH_3)
	^1H NMR (300 MHz, $(CD_3)_2CO$) δ 9.81 (br s, 1 H, N*H*), 9.75 (s, 1 H, C*H*O), 3.75 and 3.28 (dd, J = 13.0, 6.3 Hz, 1 H; dd, J = 13.0, 6.3 Hz, 1 H, NCH_2), 3.36 (m, 1 H, C*H*(Me)CO), 2.93 (s, 6 H, $N(CH_3)_2$), 1.37 (d, J = 7.4 Hz, 3 H, $CH(CH_3)$)
	^1H NMR (300 MHz, $(CD_3)_2CO$) δ 9.64 (s, 1 H, C*H*O), 9.43 (br s, 1 H, N*H*), 3.63 (s, 2 H, $NCH_2C(Me)_2$), 2.92 (s, 6 H, $N(CH_3)_2$), 1.39 (s, 6 H, $C(CH_3)_2CO$)

Table V (Continued)

compd	NMR data
	^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 9.75 (s*, 1 H, C*H*O), 3.76 (dd, J = 6.5, 6.4 Hz, 1 H, NCH_2C), 3.43–3.24 (m, 2 H, NCH_2C*H*(Me)), 2.95 (s, 6 H, N(CH_3)$_2$), 1.37 (d, J = 7.3 Hz, 3 H, CH_3)[a]
	^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 10.83 (br s, 1 H, N*H*), 9.60 (d, J = 0.7 Hz, 1 H, C*H*O), 7.91 (d, J = 8.4 Hz, 2 H, Ar*H*), 7.42 (d, J = 7.9 Hz, 2 H, Ar*H*), 3.58 (dq, J = 7.6, 0.6 Hz, 1 H, C*H*(Me)CO), 2.43 (s, 3 H, ArCH_3), 1.23 (d, J = 7.2 Hz, 3 H, CH(CH_3))
	^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 10.36 (br s, 1 H, N*H*), 9.55 (s, 1 H, C*H*O), 7.88 (d, J = 7.7 Hz, 2 H, Ar*H*), 7.41 (d, J = 8.1 Hz, 2 H, Ar*H*), 2.42 (s, 3 H, ArCH_3), 1.32 (s, 6 H, C(CH_3)$_2$)
	^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 10.58 (br s, 1 H, N*H*), 7.91 (d, J = 8.1 Hz, 2 H, Ar*H*), 7.44 (d, J = 8.2 Hz, 2 H, Ar*H*), 6.62 (s*, 1 H, C=C*H*O), 2.43 (s, 3 H, ArCH_3), 1.58 (br s, 6 H, C=C(CH_3)$_2$)[a]
	^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 9.60 (d, J = 0.7 Hz, C*H*O), 7.91 (d, J = 8.3 Hz, 2 H, Ar*H*), 7.42 (d, J = 8.2 Hz, 2 H, Ar*H*), 3.61 (dq, J = 7.2, 0.7 Hz, 1 H, C*H*(Me)), 2.43 (s, 3 H, ArCH_3), 1.23 (d, J = 7.32 Hz, 3 H, CH(CH_3))
	^{1}H NMR (500 MHz, $(CD_3)_2CO$, −40 °C) δ 6.72 (s, 1 H, O*H*), 5.45, (t*, J = 11.1 Hz, 1 H, H_2C=C*H*), 4.25 and 4.13 (d, J_{Rh-H} = 7.9 Hz, 1 H; d, J_{Rh-H} = 14.7 Hz, 1 H, H_2C=C), 3.87 (m, 2 H, CH_2O), 2.5–1.0 (m, cyphos and H_2C=CHCH_2)[a,b] ^{31}P NMR (202 MHz, $(CD_3)_2CO$, −40 °C) δ 91.25 (dd, J_{Rh-P} = 185.0 Hz, J_{P-P} = 25.9 Hz), 76.88 (dd, J_{Rh-P} = 162.8 Hz, J_{P-P} = 25.9 Hz)

[a]* Shows fine coupling. [b] Unable to decouple vinyllic methylene group; therefore, unable to distinguish between Rh and vinyllic methylene proton coupling.

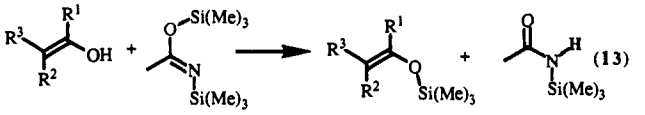
π–σ–π interconversion is fast relative to hydride transfer (Curtin–Hammett conditions), the kinetic proportions of the enol isomers would depend on the relative rates of hydride transfer. If, however, the π–σ–π interconversion is slow relative to hydride transfer, then the kinetic ratio would depend on the relative proportions of the π-allylic intermediates. We can distinguish between whether the stereoselective step involves the differential hydrogen atom abstraction and whether the proportion of enol isomers is a consequence of π–σ–π interconversion by the sequence illustrated in Figure 6.

(*Z*)- and (*E*)-crotyl alcohol each give two different π-allyl structures depending on which of the hydrogen atoms is abstracted. Thus, the (*E*)-crotyl alcohol can give a syn–syn and a syn–anti(OH) π-allyl species, whereas the (*Z*)-crotyl alcohol can give an anti–anti and anti(CH_3)–syn π-allyl intermediate. Hydrido addition to these intermediates generates *Z*- and *E*-enols from either crotyl alcohol isomer. If the hydrido-π-allyl intermediates have time to equilibrate by the π–σ–π mechanism (Figure 6), then the ratio of *Z*- and *E*-enols will be the same irrespective of the structure of the crotyl alcohol substrate. That is, the system will lose all memory of its structural antecedents. On the other hand, if π–σ–π rearrangement is slow or does not occur during catalysis, then the ratio of *Z*- and *E*-enols will, in principle, depend on the structure of the crotyl alcohol substrate. The experiment was performed with use of the diphos catalyst. We find that (*E*)-crotyl alcohol gives 54% of the *E*-enol and 46% of the *Z*-enol, whereas the (*Z*)-crotyl alcohol gives 75% of the *E*-enol and 25% of the *Z*-enol. These ratios are initial kinetic values obtained before any ketonization of the enols had occurred. The *Z*- and *E*-enols ketonize at different rates; hence, it was important to obtain initial ratios. We conclude, therefore, that little or no observable π–σ–π isomerism occurs during catalysis. It should be noted, however, that this experiment only distinguishes between syn and anti arrangements of the hydroxyl group of the putative π-allyl intermediate. It is mute on the syn–anti relationship of the methyl group that is irrelevant to the observed enol isomer proportions. It follows that the stereoselective step is the initial hydrogen atom abstraction (eqs 11 and 12). The proportion of enol iosmers is governed by steric and, perhaps, electronic factors involved in the initial hydrogen-abstraction step.

(17) Faller, J. W.; Thomsen, M. E.; Mattina, M. J. *J. Am. Chem. Soc.* **1971**, *93*, 2642.

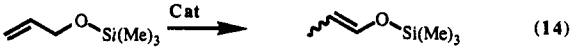
Chemical Reactions of Enols

Since under the present catalytic methods of generation enols slowly ketonize, it would be advantageous if a mild, neutral, and rapid method were found to trap them in a stable form. The readily available reagent, *N*,*O*-bis(trimethylsilyl)acetamide was found to be effective (eq 13). Since the *O*-trimethylsilyl group



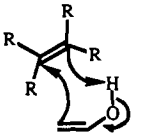
(13)

reacts faster than the *N*-trimethylsilyl group, addition of 1 mol equiv of the silylating reagent effectively trapped most of the enol present. The product is stable, and it can be catalytically generated from the silylated allylic alcohol (eq 14) but in different *E* and *Z* ratios (~2:1 for both the diphos and cyphos catalysts).



(14)

The present catalytic method, unlike other approaches, provides enols in synthetically useful amounts in aprotic solvents. It was therefore of interest to investigate the chemistry unique to enols under these conditions. The distinguishing feature of enols as opposed to enoltes, enol ethers, enol acetates, etc., is the presence of a hydroxyl proton, and we supposed that this proton would be a key element in the reactivity patterns of enols. The hydroxyl proton of enols in reactions with unsaturated substrates is envisaged as engaging in the ene mechanism shown in **13**. We have tested this hypothesis with three activated unsaturated substrates.

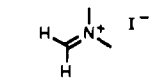
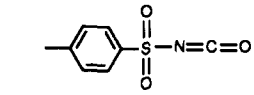
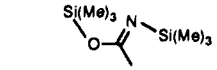
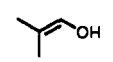
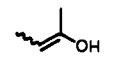
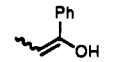
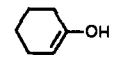


13

It is known[18] that tetracyanoethylene reacts with ethyl vinyl ether to give the cyclobutane via a zwitterionic intermediate (eq

(18) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117.

Table VI. Reactions of Enols and the Yields of Products (%)[a]

enol	TCNE[b]			
	22.4[c]	71	43	94
	95	92	76	
	86	95	46[d]	92
				63
				64
				90

[a] Reactions were virtually instantaneous in all cases. [b] Reaction carried out in THF-d_8. [c] Remainder of enol is ketonized unless stated otherwise. [d] 54% $TolS(O)_2N(H)CO_2CH{=}C(Me)_2$ remainder. [e] Note the higher yields obtained with the –OD enol.

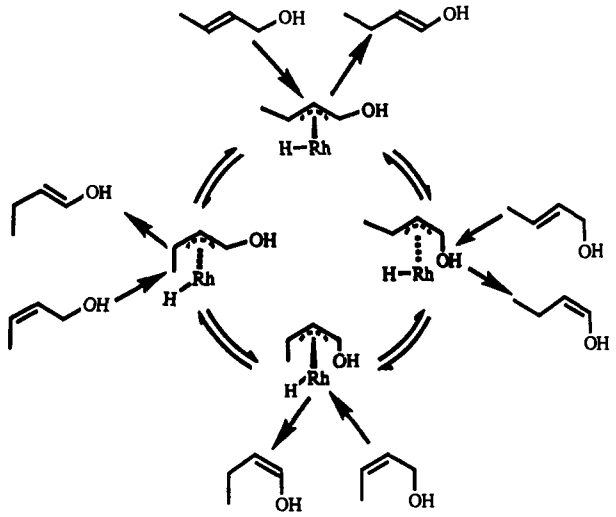
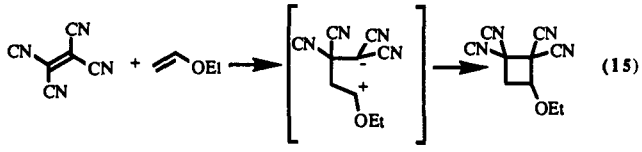
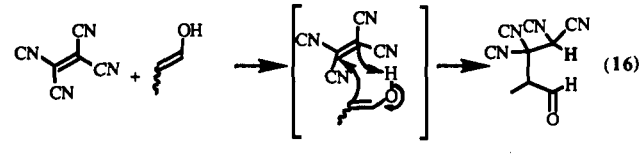


Figure 6. Illustration of the possible π-allylic intermediates derived from (*Z*)- and (*E*)-crotyl alcohol, the enol products derived from these intermediates, and the π-allylic equilibrium cycle.

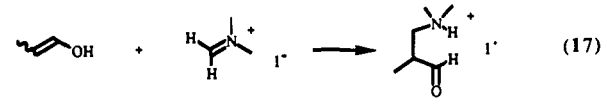
15). According to the ene mechanism, however, the corresponding reaction with the enol from allyl alcohol should give the noncyclic aldehyde (eq 16). Indeed it does. The two other substrates



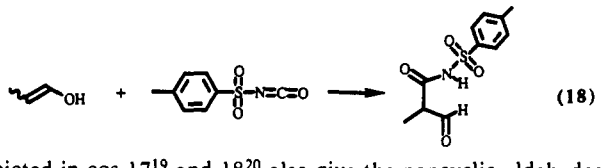
(15)



(16)

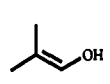


(17)

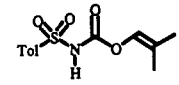


(18)

depicted in eqs 17[19] and 18[20] also give the noncyclic aldehydes as dictated by the ene mechanism. These reactions are likely to be sensitive to steric hinderance, and we investigated this effect with the enol **14**. The electrophilic reagents depicted in eqs 16 and 17 reacted with **14** to give the ene products, but the isocyanate (eq 18) gave equal amounts of the ene product and the enol ester **15**. Presumably, the appearance of **15** is a consequence of steric



14



15

hinderance. The structures of the products derived from the enols of propanal were determined by ^1H NMR with use of the all-hydrogen enols and the deuterated enol **8**. The deuterium appears in the positions expected for the ene mechanism. We note, however, that although the concerted ene mechanism is attractive, the process could be a nonconcerted mechanism.

Concluding Discussion

The present catalytic method is the most general and effective method of generating a variety of enols in aprotic solutions. This work discloses that simple enols are stable to a hitherto unsuspected extent under antiseptic aprotic conditions. Consequently, the present method provides a simple and convenient entry into the study of the physical and chemical properties of simple enols.

Experimental Section

^1H NMR spectra were measured on General Electric (GE) GN 500, GN 300, QE 300, Nicolet NTC 200, and Chicago-built 500 Fourier transform spectrometers operated at 500.1, 300.5, 300.2, 200.1, and 487.0 MHz, respectively. ^2H NMR spectra were measured on GE GN 300 and Varian XL-400 Fourier transform spectrometers operating at 46.1 and 61.4 MHz, respectively. ^{31}P NMR spectra were measured on a GE GN 500-MHz spectrometer operating at 202.4 MHz. ^1H and ^2H NMR chemical shifts were recorded relative to TMS. ^{31}P NMR data were measured relative to an 85% H_3PO_4 external reference. All glassware and syringes were treated successively with 0.1 N HCl, EtOH, NH_4OH/EtOH, and EtOH and dried to remove any trace acid, base, or H_2O. The acetone-d_6 (99.5 atom % D, Aldrich) was distilled from 3-Å molecular sieves, and the THF-d_8 (99.5 atom % D, Aldrich) was distilled from K/Ph_2CO under argon before use. The rhodium complexes [Rh(diphos)]$_2(ClO_4)_2$,[13] [Rh(cyphos)(NBD)]ClO_4,[13] [Rh(dppp)(NBD)]ClO_4,[13] [Rh(dppb)(NBD)]ClO_4[13] and [Rh((*S*)-binap)(NBD)]ClO_4[21] and the substrates $CH_2{=}C(Ph)CH_2OH$,[22] *cis*-$(CH_3)CH{=}CHCH_2OH$,[23] $CH_2{=}C(OEt)CH_2OH$,[24] $CH_2{=}CHCH(Ph)OH$,[25] and $CH_2{=}CHCD_2OH$[26] were prepared by published procedures. 1-Cyclohexenemethanol

(19) See: Roberts, J. L.; Borromeo, P. S.; Poulter, C. D. *Tetrahedron Lett.* **1977**, 1621.
(20) See: Ojima, I.; Inaba, S.; Nagai, Y. *Chem. Lett.* **1974**, 1069.
(21) Miyashita, A.; Takaya, H.; Souchi, T.; Noyori, R. *Tetrahedron* **1984**, *40*, 1245.
(22) Gassman, P. G.; Harrington, C. K. *J. Org. Chem.* **1984**, *49*, 2258.
(23) Moreno-Manas, M.; Trius, A. *Tetrahedron* **1981**, *37*, 3009.
(24) Trost, B. M.; Curran, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 5699.
(25) Duveen, D. I.; Kenyon, J. *J. Chem. Soc.* **1939**, 1697.

was prepared by $LiAlH_4$ reduction of the corresponding methyl ester (Aldrich). The remaining substrates were purchased from Aldrich, except *trans*-$(CH_3)CH{=}CHCH_2OH$ (Fluka, contained ~5% of the cis isomer). All substrates were distilled from 3-Å molecular sieves under either argon or vacuum (0.1 mmHg) and stored under argon. The *N*,*O*-bis(trimethylsilyl)acetamide, *p*-toluenesulfonyl isocyanate, and tetracyanoethylene (TCNE) were used as supplied (Aldrich), except that TCNE was recrystallized from hot chlorobenzene before use.

Preparation of $CH_2{=}CHCH_2OD$. A solution of allyl alcohol (18.4 mL, 270 mmol) in dry Et_2O (50 mL) was added dropwise over 2.25 h to EtMgBr (1.5 M in Et_2O, 200 mL, 300 mmol) under argon. The slightly cloudy mixture was then quenched by the addition of D_2O (16.2 mL), and the resultant mixture was refluxed for 0.5 h. The clear supernatant was removed by cannula and the white residue extracted with Et_2O (2 × 75 mL, Et_2O extract removed by cannula). The Et_2O was removed by careful distillation and the residue distilled through a vacuum-jacketed Vigreux column, yielding allyl alcohol-*d* (1.98 g, 11% yield, bp 98-99 °C). A ^1H NMR (acetone-d_6; 200-MHz) spectrum showed the residual OH to be ~6%.

Catalytic Runs. Typically, $[Rh(diphos)]_2(ClO_4)_2$ (0.6 mg, 9.987 × 10^{-4} mmol) was dissolved in acetone-d_6 (0.6 mL) under argon. The substrate (9.987 × 10^{-2} mmol, 100 equiv) was then added via syringe. The reactions were monitored by NMR spectroscopy. The [Rh(diphosphine)(NBD)]$^+$ was hydrogenated to the [Rh(diphosphine)(sol)$_2$]$^+$ species as follows: the [Rh(diphosphine)(NBD)]$^+$ complex was suspended in the solvent, and H_2 was bubbled into the solvent for 3 min. The gas flow was stopped, and the NMR tube was shaken for 3 min. This procedure was repeated twice to give clear solutions of the solvento complexes. The solutions were then purged with argon, the substrate was added, and the catalysis was monitored by NMR. The results are summarized in Tables I and II. The ^1H and ^2H NMR spectra are presented in Table V. The ^1H NMR assignments are based on comparison with published spectra (where available), on analogies with the corresponding trimethylsilyl ethers, and on the usual principles of NMR spectroscopy. The relevant literature references are given in Table V. The enantiomeric excess from the [Rh((*S*)-binap)(S)$_2$]$^+$ catalyzed ketonization of the enol **11** was determined by the method outlined previously.[27]

[Rh(cyphos)($CH_2{=}CHCH_2CH_2OH$)](ClO_4)·3. [Rh(cyphos)(NBD)]ClO_4 (8.29 mg, 1.157 × 10^{-2} mmol) was partially dissolved in acetone-d_6 (0.6 mL) under argon. A cycle of bubbling hydrogen gas through the mixture for 3 min followed by shaking for 3 min was repeated three times to dissolve and hydrogenate the catalyst precursor. Argon gas was then bubbled through the solution for 5 min to remove the excess of hydrogen gas. The solution was cooled to -40 °C, and $CH_2{=}CHCH_2CH_2OH$ (0.77 mg, 1.068 × 10^{-2} mmol, 0.93 equiv) was added to the mixture via syringe. Integration of the ^{31}P NMR signals indicated that 85% of the Rh was in the form of the adduct 3; the remainder was an unidentified species, believed to be bridging hydride complexes observed when an excess of hydrogen gas is used to hydrogenate the NBD complex at high [Rh].[15] This ratio is reflected in the ^1H NMR spectrum as well. The NMR data are presented in Table V. ^1H NMR assignments are based on decoupling experiments and the usual principles of NMR spectroscopy. The compound was relatively stable, decomposing ~13% after 22 min at 20 °C.

Chemical Reactions. The catalysis to generate the enol was performed as described above. Carbon monoxide was bubbled through the solution for 2 min to deactivate the catalyst at the point when all of the allylic alcohol was consumed (see Table I). The reagent (9.987 × 10^{-2} mmol, 1 equiv) was then either injected (*N*,*O*-bis(trimethylsilyl)acetamide, *p*-toluenesulfonyl isocyanate) or added as a solid. The yields based on the amount of enol originally present in solution are summarized in Table VI. The NMR data are summarized in Table V. The assignments are based on decoupling experiments, deuterium labeling, the usual principles of NMR spectroscopy, and, where possible, comparison to published data. The relevant references are given in Table V.

Acknowledgment. This work was supported by grants from the National Institutes of Health.

(26) Schuetz, R. D.; Millard, F. W. *J. Org. Chem.* **1959**, *24*, 297.
(27) Fraser, R. R.; Petit, M. A.; Saunders, J. K. *J. Chem. Soc., Chem. Commun.* **1971**, 1450.
(28) Capon, B.; Siddhanta, A. K. *J. Org. Chem.* **1984**, *49*, 255 (for enol). Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066 (for trimethylsilyl ether).
(29) Hanack, M.; Märkl, R.; Martínez, A. G. *Chem. Ber.* **1982**, *115*, 772 (trimethylsilyl ether).
(30) Schraml, J.; Šraga, J.; Hrnčiar, P. *Collect. Czech. Chem. Commun.* **1983**, *48*, 3097 (for trimethylsilyl ether). See ref 3 for spectrum of enol.
(31) Birkofer, L.; Dickopp, H. *Chem. Ber.* **1969**, *102*, 14 (trimethylsilyl ether).
(32) Stang, P. J.; Mangum, M. G.; Fox, D. P.; Haak, P. *J. Am. Chem. Soc.* **1974**, *96*, 4562 (trimethylsilyl ether).
(33) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324 (trimethylsilyl ether).
(34) Rasmussen, J. K.; Hassner, A. *J. Org. Chem.* **1974**, *39*, 2558 (trimethylsilyl ether).
(35) Heathcock, C. H.; Davidsen, S. K.; Hug, K. T.; Flippin, L. A. *J. Org. Chem.* **1986**, *51*, 3027.

Solvent, Counterion, and Secondary Deuterium Kinetic Isotope Effects in the Anionic Oxy-Cope Rearrangement

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Abstract: The potassium and sodium alkoxides of 3-methyl-1,5-hexadien-3-ol follow first-order kinetics in the process of undergoing the anionic oxy-Cope rearrangement in tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO). The first-order rate constant for the rearrangement of the potassium alkoxide in DMSO is ca. 1000 times faster than that in THF, as is the first-order rate constant in THF in the presence of 1 equiv or excess 18-crown-6. The rate constants in THF are independent of initial alkoxide concentration; in contrast, the first-order rate constants in DMSO are inversely proportional to the initial alkoxide concentration, and addition of potassium salts to the DMSO solution results in a retardation of rearrangement rate. Addition of $^1/_4$ and $^1/_2$ equiv of 18-crown-6 in THF gave first-order behavior only over the first 25% of reaction with an initial rate constant linearly related to that with 1 equiv of crown ether. Secondary deuterium kinetic isotope effects have been determined at the bond-breaking and bond-making sites in the Cope rearrangement of the potassium alkoxide in THF, in THF in the presence of 18-crown-6, and in DMSO. The isotope effects indicate a highly dissociative transition state with substantial bond breaking of the C3-C4 bond and little bond making between the allylic termini (C1 and C6). The effects of aggregation and ionic dissociation are discussed in the context of mechanistic pathways proposed for the rearrangement in THF and in DMSO.

In 1975, Evans and Golob reported the remarkable rate acceleration for the Cope rearrangement of the potassium alkoxide of alcohol **1** of 10^{10}-10^{17} relative to that for the alcohol itself.[1] In general, hydroxy and alkoxy substitution at C3 of 1,5-dienes affect the rate of thermal sigmatropic 3,3 rearrangements only minimally,[2-4] while a simple change of the hydroxyl substituent

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(1) Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765.

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