Tetrahedron Vol. 47, No. 6, pp. 949-960, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00

Deuterium Isotope Studies of the Dehydration Alcohols by Reaction with Triphenylphosphine-Tetrachloromethane

Hossein A. Dabbagh[1]*, Boris Franzus[2a], Thomas T.-S. Huang[2], and Burtron H. Davis[1]*

1. Center for Applied Energy Research, University of Kentucky, 3572 Iron Works Pike, Lexington, KY 40511-8433

2. Department of Chemistry, East Tennessee State University, Johnson City, TN 37614

(*Received in USA* 10 *October* 1990)

ABSTRACT - The reactions of 2-butanol, 2-butanol-2d_1, erythro-2-butanol-3d_1 (EB), 2-methyl-2-propanol (2M2P), and 1,1,1,3,3,3-hexadeuterio-2-methyl-2-propanol (HDMP), respectively, with CCl_4, and Ph_3P in a polar or non-polar solvent in the temperature range of 36-85°C was studied. For 2-butanol the fraction of dehydration products increased with temperature; the opposite temperature effect was observed for (2M2P). Dehydration was the dominant pathway for (2M2P) (85-95%) but substitution (of OH by Cl) was dominant for 2-butanol (75-95%). Deuterium retention in the butenes from the conversion of (EB) indicated that 98% or more of the dehydration followed an anti-elimination pathway, and there was a preference for Saytzeff elimination. An isotope effect for deuterium elimination (k_H/k_D) for the alkene-forming step for (EB) and (HDMP) was about 2.0, and neither temperature nor solvent polarity appeared to have an effect on (k_H/k_D) in the range investigated. Surprisingly, there was an isotope effect for the relative rate of the formation of alkyl halide from (EB) but not from (HDMP).

INTRODUCTION

One of the more elegant methods for the formation of primary or secondary alkyl chlorides involves the reaction of the corresponding alcohol, a trialkyl or triarylphosphine, and tetrachloromethane[1a-d]. The reaction proceeds with high conversion and in high yield[2,3a-c].

The mechanism of the displacement of OH by Cl in the reaction of triphenylphosphine (Ph_3P) and CCl_4 with alcohol includes two pathways[4a-d] (see Scheme I):

Scheme I

Path A: $Ph_3P + CCl_4 \rightarrow [Ph_3PCl]^+CCl_3^- \xrightarrow{ROH} [Ph_3POR]^+Cl^- + CHCl_3$

Path B: $Ph_3P + CCl_4 \rightarrow [Ph_3PCCl_3]^+Cl^- \xrightarrow{Ph_3P} Ph_3PCl_2 + Ph_3PCCl_2$

$Ph_3PCl_2 + ROH \rightarrow [Ph_3POR]^+Cl^- + HCl$

---

* **Deceased**

Both pathways have a common alkoxyphosphonium intermediate II which collapses to triphenylphosphine oxide and alky halide: $[Ph_3POR]^+Cl^- \rightarrow Ph_3P = O + RCl$.

The relative rates of intermediate formation $[Ph_3PCl]^+CCl^-_3$ are primary > secondary > neopentyl; the relative rates of intermediate decomposition for substitution follow the order primary > secondary > neopentyl[1a]. Furthermore, the intermediate formed from neopentyl alcohol decomposes bimolecularly in acetonitrile, and not unimolecularly as it does in $CDCl_3$[1c]; this kinetic order for substitution is not consistent with a pericyclic pathway which is relatively insensitive to large variations in solvent polarity[5a], but is consistent with an ion-pair mechanism[1d]. Weiss and Snyder, in several papers[3b-c], reported on their observations which showed the ease of formation of chlorides with inversion of configuration. Cyclohexanol reported by Tőmőskőzi et al.[4b] to produce 80 and 76% cyclohexyl chloride, respectively.

With tertiary alcohols elimination is a dominant reaction. Dehydration, while not the dominant reaction pathway for secondary alcohols, does occur as a minor reaction pathway. Appel and Wihler[4d] found that when intermediate III was treated with cyclohexanol, it resulted in 55% cyclohexene. They also reported that the reaction of 2-butanol with Ph_3P-CCl_4 reagent produced 1-butene. Since the details of the elimination have not been emphasized, the present investigation utilized deuterium labeled (2M2P) and 2-butanol to address this issue.

RESULTS

Since dehydration, in some cases, could be the major reaction pathway there was concern about the possibility of the reverse reaction, the addition of HCl to the alkene product. To prevent this from happening, a 10-20% molar excess of 2,6-di-tert-butylpyridine (DTBP) was added to the mixture to react with HCl as it formed. Brown's work[6] shows that DTBP is a sufficiently strong a base to react with HCl but, at the same time, has sufficient steric hindrance to prevent it from effecting the elimination of HCl from $(CH_3)_3CCl$. Thus, we found that $(CH_3)_3CCl$, in the presence of DTBP, did not undergo detectable elimination during 8 hours. In a similar experiment it was shown that DTBP does not cause dehydration of the reactant, (2M2P). However, the effect of DTBP and/or the hydrochloride on the intermediate $[RO^+PPh_3Cl^-]$ is not known at this time. In summary, these experiments confirm that DTBP is not able to convert an alcohol nor alkyl halide to an alkene.

The conversion of HDMP proceeds through the following reactions:

$$(CD_3)_2CH_3COH + CCl_4 + Ph_3P + DTBP \rightarrow [Ph_3POC(CH_3)(CD_3)_2]^+Cl^- + CHCl_3 + [Ph_3PCHCl_2]^+Cl^- + [Ph_3PCH_2Cl]^+Cl^-$$

$$[Ph_3POC(CH)_3(CD)_3]_2{}^+Cl^- \rightarrow (CD_3)_2C{=}CH_2 + (CD_3)(CH_3)C{=}CD_2 + (CD_3)_2CH_3CCl + (Ph)_3P{=}O + DTBP \cdot HCl + DTBP \cdot DCl$$

As expected, the total conversion increased with increasing temperature. The percentage of elimination products decreased slightly (about 5%) with increasing temperature over the range used

for this study (36 to 85°C). The same percentage of elimination occurred in CCl_4 alone or CCl_4-toluene mixtures. Likewise, acetonitrile, a more polar solvent, gave results that followed the trend of the two nonpolar solvents. The same results (figure 1) were observed in the conversion with both labeled and unlabeled (2M2P) at four temperatures. In these runs mass balance were 95% or better.

Values of k_H/k_D for alkene formation at various temperatures are shown in Table I for the dehydration of HDMP in three solvent mixtures. The values of k_H/k_D were determined from the deuterium content of the 2-methylpropene formed; data from mass spectrometry and nmr were consistent. The average value of k_H/k_D for the 11 runs was 1.97; eight values are within $\pm$ 0.04 (1σ) and all values are within $\pm$ 0.08 (2σ). Thus, within experimental error the values of k_H/k_D, just as the percentage of elimination, are independent of temperature and solvent.

Table I
Effect of Temperature and Solvent on the Kinetic Isotope Effect in the Reaction of 1,1,1,3,3,3-Hexadeuterio-2-methyl-2-propanol with Ph_3P-CCl_4

Temperature, °C[a]	Solvent[b]	Mole % Elimination[c]	$(k_H/k_D)^c$
36	[d]	92	2.05
45	CCl_4	--	1.93
55	CCl_4	90	1.91
58	[d]	89	2.00
65	CCl_4	--	1.95
75	CCl_4	--	2.00
80	[d]	86	1.97
85	Acetonitrile	85	1.99

a Temperature $\pm$ .3°C; b Excess carbon tetrachloride was used in all runs; c Average of two experimental determinations; d Carbon tetrachloride-toluene (1:1).

For the conversion of 2-butanol-3d_1, the following applies:

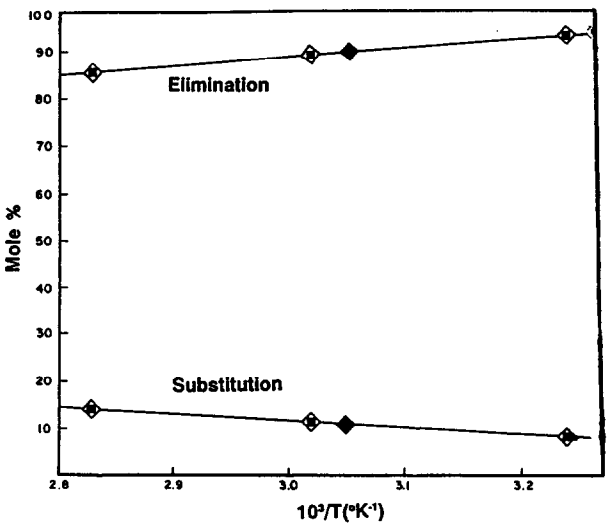
$$CH_3CHDCHOHCH_3 + CCl_4 + Ph_3P \rightarrow [Ph_3P\text{-}OC_4H_8D]^+Cl^- + CHCl_3 + [Ph_3PCH_2Cl]^+Cl^-$$

$$[Ph_3POC_4H_8D]^+Cl^- \rightarrow CH_3CH{=}CHCH_3 + CH_3CD{=}CHCH_3 + CH_3CHDCH{=}CH_2 + CH_3CHDCHClCH_3 + Ph_3P{=}O + DTBP\cdot HCl + DTBP\cdot DCl$$

or $CH_3CH_2CDOHCH_3 + CCl_4 + Ph_3P \rightarrow [Ph_3P\text{-}OC_4H_8D]^+Cl^- + CHCl_3 + [Ph_3PCH_2Cl]^+Cl^-$

$$[Ph_3POC_4H_8D]^+Cl^{-3} \rightarrow CH_3CD{=}CHCH_3 + CH_3CH_2CD{=}CH_2 + CH_3CH_2CDClCH_3 + PH_3P{=}O + DTBP\cdot HCl$$

First, the data summarized in figure 2 and Table II show that there is an isotope effect for one or more of the reaction pathways that determines the dehydration-substitution selectivity. The fraction of dehydration for the 2-butanols is in the range of 5 to 27% in contrast to 85-92% obtained with the tertiary alcohol. For the secondary alcohol there is an increase in the elimination percentage with an increase in temperature, again in contrast to the results with HDMP. Finally, the experimentally determined isotope effect, k_H/k_D, for elimination from 2-butanol-3d_1 is 2.17 $\pm$ 0.09 for the three temperatures. Considering the experimental error, as discussed above for (2M2P), the isotope effect may be considered to be essentially constant within this temperature range.



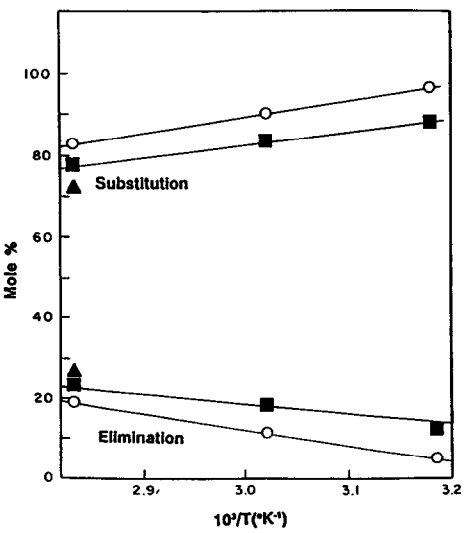


Figure 1 (left). Reaction of CCl_4-triphenylphosphine-2,6-di-tert-butyl pyridine with 2-methyl-2-propanol in toluene (◇) and 1,1,1,3,3,3-hexadeuterio-2-methyl-2-propanol in toluene (■) or 2-methyl-2-propanol in tetrachloromethane (◆).

Figure 2 (right). Effect of temperature on elimination vs. substitution for the reaction of 2-butanol (■) or erythro-2-butanol-3d_1 (○) 2-butanol-2d_1 (▲) with tetrachloromethane-triphenylphosphine-2-6, di-tert-butylpyridine in toluene.

For alkene formation from the dehydration of 2-butanol-2-d_1, there should not be a primary isotope effect, and k_H/k_D is observed to be 1.0. In the case of (EB), the isotope effect, k_H/k_D, varies from 2.08 (40°C) to 2.26 (80°C) (Table II); in this range the isotope effect has little, if any, dependence upon temperature. Thus, for elimination from (EB), the isotope effect for alkene formation is similar to that observed for HDMP.

Table II

Kinetic Isotope Effect and Elimination Products for the Reaction of 2-butanol with Triphenylphosphine-Tetrachloromethane or Sulfuric Acid

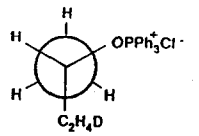
Reagents/ Temp.[b]	Alcohol	Elimination % Anti	Relative Yields of Butenes[a] % 1-	Trans-2	Cis-2	k_H^c / k_D
d/40	3-d_1[e]	> 98	18(100)[g]	38(2)[g]	44(100)[g]	2.08
	d_o[f]	---	14	56	30	
d/58	3-d_1	> 98	20(100)[g]	37(2)[g]	43(100)[g]	2.17
	d_o	---	15	56	29	
	3-d_1	> 98	22(100)[g]	36(3)[g]	42(100)[g]	2.26
d/80	d_o	---	16	55	29	1.00
	2-d_1[h]	---	14(97)[g]	56(100)[g]	30(100)[g]	
	3-d_1	60	7(75)[g]	58(33)[g]	35(49)[g]	0.82
i/80	d_o	--	11	53	36	0.96
	2-d_1	--	11(82)[g]	54(94)[g]	35(95)[g]	

(a) average of two runs (2-5% error); (b) Temperature deviation $\pm$ .3°C; (c) $k_H/k_D = [t/(1+c)d_o]/[t/(1+c)d_1]$; (d) Ph_3P/CCl_4/2,6-di-tert-butylpyridine; (e) erythro 2-butanol-3-d_1; (f) 2-butanol; (g) Deuterium content (%) given in parenthesis (corrected for ^{13}C and 2% isotope impurity); (h) 2-butanol-2d_1; (i) Sulfuric acid.

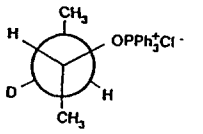
DISCUSSION

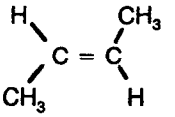
The dehydration products for 2-butanol are in the range of 5-27% and increase with an increase in temperature; the opposite temperature effect is observed for (2M2P) where the fraction of dehydration is in the range of 85-92%.

The retention (or elimination) of deuterium in the three butene isomers from the reaction of (EB) with Ph_3P-CCl_4-DTBP indicates that dehydration follows greater than 98% anti-elimination type mechanism with k_H/k_D nearly 2 (Table II). Proton-deuterium exchange does not appear to occur to a measurable extent. Thus, anti-elimination leads to the products indicated below for the conversion of (EB):

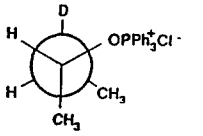


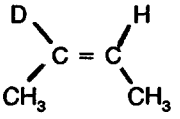
$$\longrightarrow \quad CH_3CHDCH = CH_2 \qquad (1a)$$





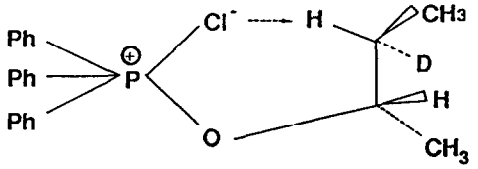
(1b)





(1c)

A possible syn elimination mechanism involves a thermal pericyclic reaction[7] wherein the P-Cl bond is broken in concert with C-H (or C-D) bond formation:



(2)

The data clearly eliminate this mechanism for the secondary alcohol and, thus, agree with the earlier rejection of this intermediate on other grounds[1d]. The elimination pathway contrasts to the normal pyrolytic elimination where a syn reaction mechanism is the exclusive, or very dominant, reaction pathway[7].

In similar experiments, when 2-butanol-2d_1, rather than (EB) reacted with (Ph_3P-CCl_4-DTBP) essentially all of the deuterium was retained in the butene products. Both exchange and scrambling of deuterium took place when sulfuric acid, a typical Brönstead acid, was used instead of (Ph_3P-CCl_4-DTBP). Therefore, it seems reasonable to assume that almost all of the dehydration in the reaction of 2-butanol with (Ph_3-CCl_4-DTBP) proceeds via a concerted anti-elimination or tightly bonded ion pair intermediate, and not a mechanism involving a free carbocation species. A carbocation ion mechanism should apply to dehydration of this alcohol via sulfuric acid; here stereospecificity was lost and up to 25% of deuterium and proton exchange was observed.

The kinetic isotope effect (k_H/k_D) for E_2 elimination is expected to be in the range of 2-8[5c]. The value of k_H/k_D = ca. 2 falls at the lower range for a concerted E_2 elimination. This may be due to an unsymmetrical transition state during bond making and bond breaking. It is well-established that symmetrical bond making-bond breaking in the transition state produces the highest values for k_H/k_D, and that as the H-C-C-X dihedral angle deviates from 180° the value of k_H/k_D decreases. The structure for (2) represents an intermediate that would have a bent C-D-Cl or C-H-Cl bond that could cause a low k_H/k_D isotope effect for elimination.

The products from the gas phase pyrolytic elimination from 2-chlorobutane are 1-butene, 42%; cis-2-, 22% and trans-2-, 36% for reaction at 290 or 360°C[8,9]. The products in the present study, while obtained at a lower temperature, do not resemble these pyrolytic products. To the contrary, the elimination products reported in Table II resemble much more closely those obtained from the dehydration catalyzed by sulfuric acid, presumably through a carbocation mechanism. Thus, even the dehydration products from the secondary alcohol (with TPP,DTBP) may arise from an intermediate that resembles a carbocation mechanism, or at least one where product stability has a strong impact, e.g.:

$$[CH_3(CD_3)_2C]^+Cl^- \rightarrow CH_2 = C(CD_3)_2 \text{ or } CD_2 = CCH_3CD_3 + HCl \quad (3)$$

Calculations show (see Experimental) that for (2M2P), the difference between k_H/k_D for 36 and 85°C (for an activation energy difference of 1.2 kcal) should be about 1.66. This maximum change in the isotope effect was not observed. Using the experimental value of $k_H/k_D = 2$ we calculate that the effect on k_H/k_D due to temperature should be 0.18. Even this value is larger than the observed differences. The experimental k_H/k_D values were determined from mass spectrometer analysis (and FT NMR) of the recovered isobutene, and proved to be invariant with temperature (see Table 1 and 2). Either of the following may account for the invariance of k_H/k_D with temperature.

First, there may be a compensation effect between activation energy and the Arrhenius preexponential factor. This requires that A_H/A_D must increase to effectively offset the decrease due to E_{act} so that k_H/k_D remains constant[10]. While compensation factors are frequently encountered, it would be unusual to find a case where the two change to cancel each other in the reported temperature range.

Alternatively, the constancy of k_H/k_D can be rationalized by a "tunnelling effect"[11,12]. The theory and applications of the tunnel effect have been reviewed[13]. Generally one finds that intervention of a tunneling effect is manifested by an enhanced isotope effect over and above that anticipated purely by differences in zero point energies[13]. In view of our small difference in the temperature effect and the experimental uncertainties, a more detailed discussion of this topic is not merited.

Another interesting observation is the isotope effect for the substitution versus elimination reactions for the two alcohols; i.e.:

$$\text{Alkenes} \xleftarrow{k_e} [ROPPh_3]^+Cl^- \xrightarrow{k_s} RCl \quad (4)$$

The ratio k_s/k_e for the tertiary alcohol (figure 1) is not altered by isotope substitution in the beta position but does change for the secondary alcohol (figure 2) for deuterium substitution in the beta position. At the same time both alcohols exhibit a similar isotope effect (ca. 2.0) for alkene formation.

For the secondary alcohol (figure 3) elimination and substitution are viewed to occur through identical chemical species ($[R(H)OPPh_3]^+Cl^-$ or $[R(D)OPh_3]^+Cl^-$). When deuterium is present in (EB), the energy level of the structure leading to trans-2-butene, and only for the formation of this product, will be different from the corresponding structure which contains protium. Deuterium substitution therefore alters only one of the four reaction coordinate energy levels. Thus, the same absolute amount of three of the four products (2-chlorobutane-$3d_1$, 1-butene-$3d_1$ and cis-2-butene-$3d_1$) will be formed irrespective of whether the alcohol contains D or H in the beta position. The amount of trans-2-butene formed when the alcohol contains D is less than when it contains H. Thus, the deuterium effect upon the rate determining step to form trans-2-butene alters both the relative amounts of the three butenes as well as the relative amount of alkyl halide.

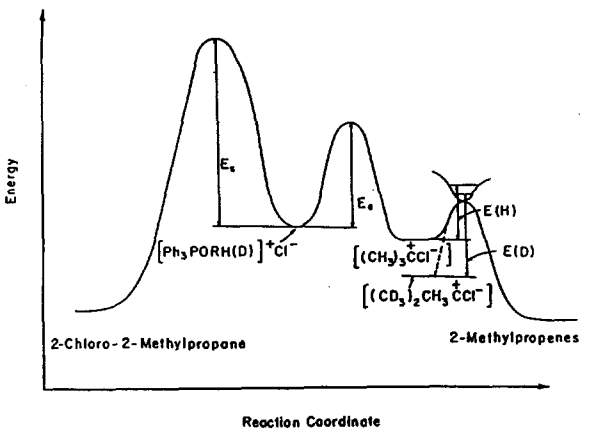


Figure 3. Schematic reaction coordinate for substitution to produce 2-chlorobutane and elimination from butenes where only the pathway leading to trans-2-butene from the deuterium labeled alcohol (E_e,D) exhibits a different activation energy than the hydrogen containing alcohol (E_e,H).

For the tertiary alcohol the situation is different; k_s/k_e is the same for $C_4H_{10}O$ and $C_4H_4D_6O$. This means that the C-D bond is not involved in the rate determining step of either reaction. On the other hand, there is an isotope effect in the step that determines whether D or H is lost in the alkene forming step of the elimination pathway. This observation can be accounted for by a reaction pathway that has two steps for the elimination reaction. The second step has a lower activation energy and determines whether a C-H or C-D bonds is broken in forming the alkene products (figure 4).

In summary, the current results show: (a) an isotope effect for elimination versus substitution selectivity for the secondary but not for the tertiary alcohol, (b) an anti-elimination mechanism for 2-butanol, and (c) a low k_H/k_D value of ca. 2 for the alkene forming reaction step. The data are

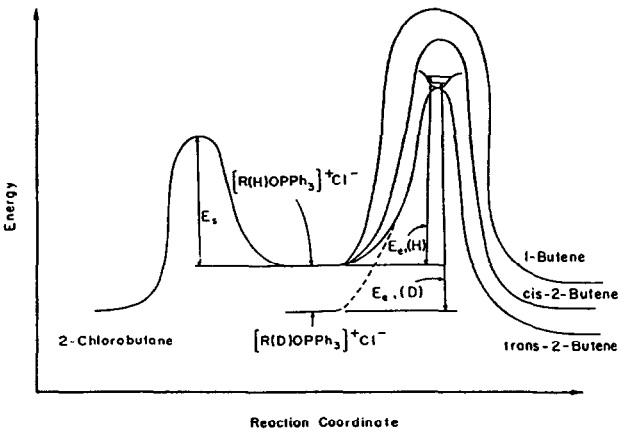


Figure 4. Schematic reaction coordinate for elimination and substitution for the tertiary alcohol, E(H) and E(D) are, respectively, the activation energies for H and D removal in a step that is faster than the rate determining step for elimination.

consistent with an ion pair intermediate provided a different reaction pathway applies for the two alcohols. Thus, for 2-butanol, elimination appears to follow a concerted type mechanism even though triphenylphosphine leaving is sufficiently advanced so that a charge becomes localized upon the alkyl group derived from the alcohol. In the case of the tertiary alcohol, the mechanism resembles, or actually involves, a carbocation-type elimination. Our results also indicate that this reaction promises to be a useful method for the synthesis of alkenes from tertiary alcohols under mild reaction conditions and provides high yields of the desired product.

EXPERIMENTAL

Mass spectra were determined with Hewlett Packard 5985 A G.C. mass spectrometer and a JEOL JMS-D100 mass spectrometer. ^{1}H NMR spectra were determined with a JEOL C-60H spectrometer. The analyses and purity evaluations of all alcohols were performed on a Perkin-Elmer 990 or Varian model 3700 gas chromatograph using respectively either a 1/8 in. x 12 ft. column, packed with 20 percent FFAP on chromosorb W, 1/8 in. x 15 m SP 1700 column, 30 m x .32 mm Supelcowax 10, 30 m x .53 mm Alteck RS2-160,or a 1/8 in. x 20 ft. silicone column. Preparatory GLC were done on a 0.5 in. x 20 ft. FFAP column on a Varian 1800 Aerograph gas chromatograph. All starting materials were obtained from Aldrich Chemicals.

Typical Reaction Procedures:

a. Preparation of Alkenes and Alkyl Halides

Into a pressure vessel (equipped with the Rotaflo stopcock), filled with 20g of 3mm glass beads was added 6.67 mmol of one of the following alcohols: 2-methyl-2-propanol, 1,1,1,3,3,3-hexadeuterio-2-methyl-2-propanol, 2-butanol, 2-butanol-2d_1, or (EB). To this was added 1.65g (8.62

mmol) 2,6-di-tert-butylpyridine, 6.00g (38.46 mmol) tetrachloromethane and 54.35 mmol of toluene or acetonitrile. This mixture was injected to a capillary GLC to obtain data to calculate the moles of alcohol using a response factor K (see calculation of K). The reaction vessel was cooled in an ice bath and 2.10g (8.02 mmol) triphenylphosphine was added. The reaction vessel was evacuated to approximately 30mm Hg at -20°C, and then allowed to warm to 10°C below the desired reaction temperature in a hot water bath. Finally, it was placed in an oil bath at the desired reaction temperature ($\pm$ 3°C) until all alcohol was converted. The volatile components were distilled from the mixture using vacuum distillation and trapped in a U-tube shape flask cooled to liquid nitrogen temperature. A small portion of this sample was subjected to GC analysis and the relative amount of substitution versus elimination was obtained from this analysis.

b. Reaction of 2-Butanol with Concentrated Sulfuric Acid in 2-Octanol

One of the following alcohols (0.67 mmol) (2-butanol, 2-butanol-2d_1, or erythro-2-butanol-3d_1) was added to the pressure vessel described above. To this was added 10 drops of concentrated sulfuric acid and 10 g (76.92 mmol) of 2-octanol. The reaction vessel was evacuated as described above and placed in an oil bath at 80 $\pm$ .3°C for 48 hours. Product work-up was described above.

c. Separation of Butenes From Less Volatile Components

The volatile mixture from a run described above was transferred into a 25 ml distillation flask connected to a mini-fractional distillation column with the receiving flask at dry-ice temperature. Butenes were distilled by immersing the reaction flask in a 40°C oil bath. Following collection, the butenes sample was subjected to GC mass spectrometric analysis.

Alternatively, the volatile products were introduced directly into an on-line capillary gas chromatograph (capable of separating the individual components as well as the butene isomers) mass spectrometer. The mass spectra of each compound was utilized to obtain of their isotopic composition. In both procedures, 10eV was utilized for the ionization.

d. Calculation of the Isotopic Composition of Butenes

d.1. Isobutylene. Peak area for m/e 61 and m/e 62 were used to calculate the kinetic isotope effect. Peak m/e 60 (M-1) was very small (< 2%). The starting alcohol, $(CH_3)(CD_3)_2COH$, has twice as many deuterium as protonium (6 D's versus 3-H's); thus, the following equation can be used to calculate the kinetic isotope effect:

k_H/k_D = (6 x peak area of m/e 62)/(3 x peak area of m/e 61)

For each temperature, the kinetic isotope effect (k_H/k_D) was then calculated for repeat analysis and the averaged values are reported.

d.2. 1-Butene (1-B), trans-2-butene (t-2-B), and cis-2-butene (c-2-B). Peak areas m/e 56 and m/e 57 were used to calculate the isotopic composition for each of the butene isomers. Peak m/e 55 (M-1) was very small (< 2%); thus, contribution of (M-1) peak (m/e 56) for C_4H_7D should likewise

be so small that it can be ignored. The kinetic isotope effect was calculated using the relative molar % butenes from Table II in the following equation:

$$k_H / k_D = \frac{[t\text{-}2\text{-}B/(c\text{-}2\text{-}B + 1\text{-}B)]_H}{[t\text{-}2\text{-}B/(c\text{-}2\text{-}B + 1\text{-}B)]_D}$$

d.3. FT NMR Analysis

A typical run was performed as discussed previously. The alkene were distilled from the other volatile components by preparative GLC and then transferred to a Pyrex tube (specially designed to hold 3 mL of solution with sealable top) containing 60 volume percent tetrachloromethane and 40 volume percent trichloromethane (d_1). The Pyrex tube was sealed and sent to Biomeasure, Inc. for analysis.

In a typical analysis the integral for CH_3 (δ = 1.70) for deuterium elimination to produce $(CH_3)(CD_3)C{=}CD_2$ was 30.0 and for the CH_2 group (δ = 4.62) in the hydrogen elimination product, $(CD_3)_2C{=}CH_2$, the integral was 44.5. To equate the ratio of elimination products to the NMR integrals, one must either multiply the CH_2 area by 3/2 or multiply the alkyl group CH_3 by 2/3 as well as make allowance for the presence of two CD_3 for each CH_3; thus, for a typical analysis using the above data the calculation becomes: $K_H/K_D = 2(30.0 \times 3/2)/44.54 = 2.02$

d.4. Correction for ^{13}C Effect on Alkene Mass Peaks

^{13}C contributes 1.12 percent/carbon to each mass peak. Thus, peak m/e 61, with four carbons, would have a ^{13}C contribution of [peak height (m/e 61) x 0.044] to peak m/e 62. This value was subtracted from peak height m/e 62 for the isotope calculation. All other deuterium analysis by MS were corrected similarly.

d.5. Expected Kinetic Isotope Effect

From reaction rate theory, the following equations apply for conversion of the deuterated and nondeuterated alcohols: $k_H = A_H \exp(-E_H/RT)$ $k_D = A_D \exp(-E_D/RT)$
If one assumes $A_H = A_D$ and $E_D - E_H = 1.2$, as is commonly done, it follows that at 85°C k_H/k_D = 5.45 and 36°C this ratio is 7.11. Thus, the difference in the isotope effect for these two temperature extremes is 1.66.

The value for the difference in activation energy used above is larger than obtained experimentally. Taking $k_H/k_D = 2$, as observed at 36°C, one calculates $E_D - E_H$ = 424 cal. Using this value for $E_D - E_H$, one calculates the difference in k_H/k_D between 36 and 85°C to be 0.18.

e. Effect of 2,6-Di-tert-Butylpyridine (DTBP) on Formation of Alkene

Into each of the two NMR tubes was added about 0.08 g (1.10 mmol) of 2-methyl-2-propanol, about 0.361 g (1.38 mmol) of triphenylphosphine, 0.650 g (4.22 mmol) of tetrachloromethane, and into one of the two tubes (0.36 g (1.88 mmol) of (DTBP) was added. The

two NMR tubes were sealed, under vacuum, and then placed in an oil bath at 65°C. Alkene was not produced in either tube after three days.

Similarly, 0.140 g (1.50 mmol) of 2-chloro-2-propane, 0.02 g (0.06 mmol) triphenylphosphine, 0.03 g (0.110 mmol) triphenylphosphine oxide, 0.94 g (6.00 mmol) tetrachloromethane and 0.15 g (0.80 mmol) of (DTBP). The NMR tube was sealed under vacuum, and then placed in an oil bath at 110°C during 8 hours. The tube was briefly withdrawn every two hours and a NMR spectra was recorded. No conversion could be observed.

f. Preparation of Starting Material.

f.1. d,ℓ-Erythro-3-deuterio-2-butanol[14]: trans-2,3-epoxybutane was reduced with $LiAlD_4$ in ethyl ether to give 72% yield of this alcohol (B.P. 97-98°C, 98 atom %D).

f.2. 2-Deuterio-2-butanol[14]: 2-butanone was reduced with an equimolar amount of $NaBD_4$ in ethyl ether to give 85% yield of this alcohol (B.P. 98.5°C, 97 atom %D).

f.3. 1,1,1,3,3,3-hexadeuterio-2-methyl-2-chloropropane (HMCP)[15]. Acetone-d_6 was reacted with methyl magnesium iodide in ethyl ether and after proper workup the (HMCP) was fractionally distilled at 78-79°C to give 68.7% yield at greater than 98% purity (GLC). Deuterium analysis of the alcohol, performed by the Yosef Nemeth Laboratories, showed it to be 98% isotopically pure.

REFERENCES

1. (a) Jones, L. A.; Sumner, Jr., C. E.; Franzus, B.; Huang, T. T.-S.; Snyder, E. I. J. Org. Chem., 1978, 43, 2821; (b) Lee, J. B. J. Am. Chem. Soc., 1966, 88, 3440; (c) Downie, I. M.; Holmes, J. B.; Lee, J. B. Chem. Ind. (London), 1966, 900; (d) Slagle, J. D.; Huang, T. T.-S.; Franzus, B. J. Org. Chem., 1981, 46, 3526.
2. Hooz, J.; Gilani; S. S. H. Can. J. Chem., 1968, 46, 86.
3. (a) Weiss, R. G.; Snyder, E. I. Chem. Commu., 1968, 1358; (b) Weiss, R. G.; Snyder, E. I. J. Org. Chem., 1970, 35, 1627; (c) Weiss, R. G.; Snyder, E. I. J. Org. Chem., 1971, 36, 403.
4. (a) Appel, R. Angew. Chem., Int. Ed. Engl., 1975, 14, 801; (b) Tőmőzkőzi, I.; Gruber, L.; Radics, L. Tetrahedron Letters, 1975, 29, 2473; (c) Harrison, C. R.; Hodge, P.; Hunt, B. J.; Khoshdel, E.; Richardson, G. J. Org. Chem, 1983, 48, 3721; (d) Appel, R.; Wihler, H.-D. Chem. Ber., 1976, 109, 3446.
5. (a) Marchand, A. P.; Lehr, R. E. in "Pericyclic Reactions"; Academic Press, New York, 1977; Vol. I, pp. 34-37; (b) Toto, D. D.; Doi, J. T. J. Org. Chem., 1987, 52, 4999; (c) Bordwell, F. G. Accounts of Chem. Res., 1970, 5, 375.
6. Brown, H. C.; Kanner, B. J. Am. Chem. Soc., 1953, 75, 3867.
7. Cristol, S. J.; Strom, R. M.; Stull, D. P. J. Org. Chem., 1978, 43, 1150.
8. Heydtmann, H.; Pinch, Z. Phys. Chem., (Frankfurt on Main), 1961, 30, 250.
9. Maccoll, A.; Stone, R. H. J. Chem. Soc., 1961, 2756.
10. Laidler, K. J. "Chemical Kinetics", 2nd Ed. McGraw-Hill Co., NY, 1965, p. 90, 251.
11. Kwart, H.; George, T. J. J. Org. Chem., 1979, 44, 162.
12. Kwart, H.; George, T. J.; Horgan, A. G.; Lin, Y. T. J. Org. Chem., 1981, 46, 1970.
13. (a) Bell, R. P. Chem. Soc. Rev., 1974, 2, 513; (b) Bell, R. P., Chem. Soc. Rev., 1972, 1, 211.
14. Brown, H. C.; Zweifel, G. J. Am. Chem. Soc., 1960, 82, 4708.
15. Dabbagh, H. A. M.S. Thesis, East Tennessee State University, 1981.