washed with water and saturated NaCl solution and dried over $MgSO_4$. The ether solvent was removed using a rotary evaporator. The nitrile products were analyzed by ^{13}C NMR spectroscopy to confirm the presence of ^{15}N in the nitrile products and by mass spectrometry to quantitatively determine the extent of ^{15}N incorporation. The error in the mass spectrometric analysis was estimated to be ±0.1% when samples were introduced using a gas expansion bulb inlet system or ±0.2% when samples were analyzed by GC–MS method. Nitrile products derived from reaction of ^{15}N terminally labeled sodium azide with **27**, **30**, and **31** were analyzed by the former method, while nitrile products derived from **25**, **26**, **28**, and **29** were analyzed by the later method. Product ratios were calculated from the $m/(m + 1)$ ratio. A spectrum of an authentic sample of the appropriate nitrile was also recorded to experimentally determine the intensity of the $m - 1$ and the $m + 1$ peaks which were used in the calculation of ^{14}N to ^{15}N ratios.

In the case of the reaction of phenylchlorodiazirine, **28**, with labeled sodium azide, approximately 25% unreacted **28** still remained after 40-h exposure to room light. At the end of this period, an aqueous workup was carried out and the benzonitrile product was separated from the unreacted **28** by silica gel chromatography.

Reaction of (*m*-Nitrophenyl)chlorodiazirine, 26, with Sodium Azide. Initiation Using the Sodium Salt of 2-Nitropropane. The sodium salt of 2-nitropropane was prepared by addition of 1.05 g of 2-nitropropane to 20 mL of 0.5 M $NaOCH_3$ in methanol. The methanol was removed using a rotary evaporator, and the solid was washed with two portions of ether. The ether was decanted and the solid was dried under vacuum to give 1.04 g (94%) of the nitronate salt **34**. This salt was relatively insoluble in DMSO-d_6.

To a stirred solution of 43.8 mg of NaN_3 in 1.8 mL of DMSO-d_6 (in the dark under N_2) was added 40.1 mg of (*m*-nitrophenyl)chlorodiazirine, **26**. The solid nitronate salt **34** (2.2 mg) was immediately added to the stirred solution. Nitrogen evolution began immediately and continued over about 5 min. After 15 min a sample was withdrawn and analyzed by ^1H NMR spectroscopy which showed no unreacted diazirine **26**. A standard aqueous workup followed using ether extraction. The ether extract was washed with a portion of water and saturated NaCl solution and dried over $MgSO_4$. Solvent removal using a rotary evaporator left 26.3 mg (88%) of *m*-nitrobenzonitrile, which was spectroscopically identical with an authentic sample.

Acknowledgment is made to the National Science Foundation for financial support of this research.

Registry No. **1**, 4222-25-7; **10**, 125330-15-6; **20**, 115127-49-6; **25**, 39184-67-3; **26**, 53442-61-8; **27**, 125330-16-7; **28**, 115127-52-1; **29**, 4460-46-2; **30**, 74671-01-5; **31**, 125330-17-8; **34**, 24163-39-1; *p*-nitrobenzonitrile, 619-72-7; *p*-nitrobenzamidine hydrochloride, 15723-90-7; sodium azide, 26628-22-8; galvinoxyl, 2370-18-5; sodium thiophenoxide, 930-69-8.

Pyrolysis of *sec*-Butyl Acetate. Is the Stereospecific Syn Elimination a Homogeneous or Heterogeneous Reaction?

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A kinetic isotope effect of ca. 2 was obtained for the pyrolysis of either 1,1,1-trideuterio-2-butyl acetate or *erythro*-2-butyl-*3*-d_1 acetate over glass beads. Under the same reaction conditions, except for the use of a high surface area silica rather than glass beads, the isotope effect was lower. With the high area silica, 2-butanol dehydration produced no isotope effect, and, in contrast to acetate pyrolysis, the silica catalyzed H–D exchange during the formation of the butene products. Butene and D_2O did not undergo exchange under the alcohol dehydration conditions. It is concluded that surface catalysis during acetate pyrolysis over low surface area glass beads does not make an important contribution but may with high surface area silica.

Introduction

The pyrolysis of esters is a well-established convenient method for the preparation of alkenes. The products are those predicted for β-elimination, and usually the products undergo minimal secondary reactions.[1] With other synthetic methods, such as catalytic dehydration of alcohols, secondary reactions may be a significant problem.[2] This reaction is also of interest from a mechanistic viewpoint, and many studies have been devoted to various aspects of the elimination pathway, for example.[1,3-6]

Maccol[7] considered this reaction to be especially attractive for study because in the gas phase it is possible to investigate the behavior of a single molecule, uninfluenced by the presence of the remainder of the system. The effect of substitution in a parent molecule upon the rate of a given reaction can thus be studied without the complications arising from the cooperative effects of the solvent, as may occur in reactions in solutions. Obviously, for this assertion to be valid surface effects of the reaction vessel must be minimal, or absent. Wertz and Allinger[8] indicated that surface effects may be a significant factor. They stated that the isomer ratios observed in the alkene products are generally inconsistent with a one-step gas-phase reaction that occurs by a cyclic transition state, but they are consistent with a surface-catalyzed reaction. These latter authors believed that, while true gas-phase reactions appear to have been observed in kinetic experiments, the experimental conditions employed in most cases where isomer ratios have been reported for the products, which are the conditions commonly used for preparative work, resulted from a surface-catalyzed reaction.

Observations which are consistent with a gas-phase mechanism for ester pyrolysis are[1,8] (1) the loss of a cis

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(1) Saunders, W. H., Jr.; Cockerill, A. F. *Mechanisms of Elimination Reactions*; John Wiley & Sons: New York, 1973; pp 377–482.

(2) For example, see: Formin, W.; Sochanski, N. *Ber.* **1913**, *46*, 246.

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(4) DePuy, C. H.; King, R. W. *Chem. Rev.* **1960**, 431.

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(6) Briggs, W. S.; Djerassi, C. *J. Org. Chem.* **1968**, *33*, 1625.

(7) Maccol, A. In *Advances in Physical Organic Chemistry*; Gold., V., Ed.; Academic Press: New York, 1965; Vol. 3, pp 91–122.

(8) Wertz, D. H.; Allinger, N. L. *J. Org. Chem.* **1977**, *42*, 698.

0022-3263/90/1955-2011$02.50/0

Table I. Butene Composition from the Conversion of 2-Butyl Acetate with Various Hydrogen Pretreated Silicas

silica	temp, K	convn, %	butenes[a] (unlabeled acetate)		
			1-	*trans*-2-	*cis*-2-
SiO_2 (380 m^2/g)	573	10	55	29	16
	623	90	61	26	13
	723	>98	46	32	22
SiO_2 (50 m^2/g)	623	95	54	28	18
	723	>98	35	25	30
SiO_2 (0.18–0.25 mm)	623	95	55	28	17
	723	>98	50	30	20
SiO_2 (3 mm)	623	90	57	28	15
	723	>98	51	31	18

[a] Experimental error 3%.

β-hydrogen is much preferred to the loss of a trans β-hydrogen, (2) rearrangement products are rare, (3) when both the cis and trans alkene can be formed by the loss of a cis β-hydrogen, the cis/trans ratio is about what would be expected on the basis of the relative stabilities of the alkenes, (4) the deuterium isotope effect shows that the β-hydrogen is lost in the slow step of the reaction, and (5) the more acidic the acid produced, or the more stable the carbonium ion that would result from alkyl-oxygen cleavage, the faster the reaction.

Wertz and Allinger[8] compared experimental cis/trans ratios obtained from the pyrolysis of several aliphatic alcohol acetates to those ratios expected, after correcting for statistical effects, on the basis of the corresponding energy differences. They contended that the data could not be explained by the generally accepted mechanism and proposed an alternative mechanism comprised of the following three steps: (1) in a rapid equilibrium step the compound is adsorbed with the ester group on the surface, (2) in a second step the ester C–O bond is broken to form a carbonium ion which is stabilized by the surface, and in so far as possible, the ion adopts a conformation which allows maximum contact between the surface and the ion (in the pyrolysis of at least some esters, this step appears to be reversible), and (3) in the rate-determining step, the carbonium ion loses a β-hydrogen to form the alkene. The steps may be more or less concerted, and the degree of concertedness may vary with the compound.

We have utilized acetate pyrolysis to synthesize isotopically labeled alkenes. In view of the importance of the pyrolytic mechanism in the development of an understanding of organic chemistry, we have obtained additional data to address the question of the extent that acetate pyrolysis can be viewed as a surface-catalyzed reaction. The approach employed was to vary the amount of silica surface in the reactor and to observe the influence of surface area on the isotope effect for elimination, the stereospecificity of the elimination reaction, and the product distribution. At the same time, we recognize the difficulties in proving that the surface does not play a role in the reaction.

Results

Data for the conversion of unlabeled 2-butyl acetate (15 to 20 wt % in 2-octyl acetate) are summarized in Table I. The data indicate that as the temperature of the conversion increases the amount of 1-butene in the products decreases. The percentage increase in *trans*- and *cis*-2-butene is about the same. The data for butene composition will vary slightly from run to run when pretreating silica from the same batch. Based upon data for the catalytic isomerization of 1-butene, a preferential formation of *cis*-2-butene from 1-butene is expected.[9]

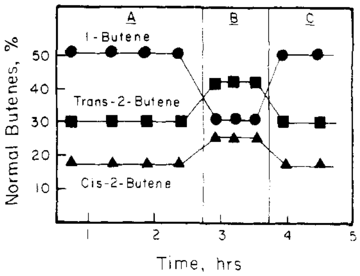

Figure 1. The normal butene distribution from the pyrolysis of an undeuterated 2-butyl acetate/2-octyl acetate mixture or 1,1,1-trideuterio-2-butyl acetate/2-octyl acetate (B) at 723 K over 3-mm Pyrex glass beads (regions A and C refer to conversions with unlabeled butyl acetate and region B to conversion of deuterated butyl acetate).

1,1,1-Trideuterio-2-butyl acetate (15 wt % in 2-octyl acetate) was converted over low surface area silica (3-mm glass beads) at 573 K; this conversion was bracketed with conversons of an undeuterated 2-butyl acetate/2-octyl acetate mixture immediately prior to and following the conversion of the labeled reactant (Figure 1). Thus, the difference in the rate of conversion of the labeled and unlabeled butyl acetate will not be due to differences in the surface of the silica. There is a significant isotope effect for the formation of butenes as the data in Tables I and II clearly show. The amount of 1-butene formed from the unlabeled butyl acetate was 55% of the butene isomers; this amount was formed both before and following the conversion of the deuterated butyl acetate. The amount of 1-butene decreased from 55 to 39% when the feed acetate mixture was switched from the undeuterated to the deuterated butyl acetate; at the same time the amount of *trans*-2-butene increased from 29 to 40% and *cis*-2-butene increased from 16 to 21%. Thus, the fractional increase (ratio of isomer from unlabeled/labeled reactant) for *trans*- and *cis*-2-butene was approximately the same; this is the anticipated result. The kinetic isotope effect for the conversion of 2-butyl acetate at 573 K is 1.9. Within the experimental error for the MS analysis, the 1-butene had lost one deuterium and the 2-butene isomers contained three deuteriums, as expected.

1,1,1-Trideuterio-2-butyl acetate was also pyrolyzed over Pyrex glass beads (3 mm) at a higher temperature, 723 K. The butenes consisted of 51% 1-butene, 31% *trans*-2-butene, and 18% *cis*-2-butene from the conversion of unlabeled butyl acetate and 30.5% 1-butene, 43.0% *trans*-2-butene, and 26.5% *cis*-2-butene for the deuterated butyl acetate (Figure 1). This corresponds to an isotope effect of 2.37. Again, the 2-butenes contained, within experimental error, three deuteriums, and 1-butene contained two deuteriums. At temperatures below 623 K the gaseous product consisted of greater than 99% butenes. With increasing reaction temperature the acetic acid decomposed during or following the pyrolysis step to produce other gaseous products; this effect was especially pronounced during the initial exposure to the reactant and decreased with continuing use. Thus at 723 K with the "fresh" 3-mm beads, the C_1 fraction was composed of 11% CO, 36% CO_2, and 53% methane; these were the only products that could be determined using this GC column. Using another GC column, it was found that the hydrocarbon fraction consisted of C_2, 10%; C_3, 8%; C_4, 72%; butadiene or another product with the same retention time, 4.4%; and C_5, 6%. Even at the highest temperature utilized, less than 2% of the C_4 products were 2-methyl-

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(9) Davis, B. H. *J. Catal.* **1979**, *58*, 493.

Table II. Butene Composition from the Conversion of Deuterium-Labeled 2-Butyl Acetate with Hydrogen Pretreated Silica

				butenes			
silica	label	temp, K	convn, %	1	*trans*-2-	*cis*-2-	$k_H{}^a/k_D$
380 m^2/g	*1,1,1*-d_3	573	10	39	40	21	1.91
380 m^2/g	*1,1,1*-d_3	623	ca. 90	57	28	15	1.26
380 m^2/g	*3*-d_1	623	>90	65	25	10	1.3
3 mm	*1,1,1*-d_3	723	>95	30.5	43.0	26.5	2.37
3 mm	*3*-d_1	623	90	64	27	9	1.78

[a] Calculated using data in Tables I and II.

Table III. Pyrolysis of 3-Methyl-2-pentyl Acetate over 3-mm Glass Beads (Pretreated in Oxygen and Then Nitrogen at 450 °C) and a Mixture of *erythro*-3-Methyl-2-pentyl Acetate (11.3 mol % in 2-Octyl Acetate)

		3-methylpentenes			octenes, mol %				
time, min	temp, K	*1*-	*trans*-2-	*cis*-2-	1-	*trans*-2-	*cis*-2-	conv 3m2p[a,f]	2-octyl[a,f] 3m2p
130	623[c]	68.0	13.0	19.0	–	–	–	25	–
360[b]	673[c]	65.0	14.0	21.0	–	–	–	~100	–
30	623[d]	70.0	26.0	4.0	47.0	37.5	15.5	–[e]	5.60[f]
60	623[d]	73.0	26.0	1.0	47.0	37.5	15.5	–[e]	5.10
120	623[d]	73.0	26.0	1.0	47.0	37.0	16.0	–[e]	4.80
160	623[d]	73.5	25.5	1.0	47.0	37.0	16.0	–[e]	4.85
233[b]	673[d]	71.0	28.0	1.0	46.0	37.0	17.0	–[g]	4.65
263[b]	673[d]	71.0	28.0	1.0	47.0	37.0	16.0	–[g]	3.80

[a] Ratio of 2-octyl acetates (2-octyl) to 3-methyl-2-pentyl acetate (3m2p) in liquid products. [b] Products were not collected during temperature increase and a 15 min following the attainment of 673 K. [c] Reactant was 3-methyl-2-pentyl acetate only. [d] Reactant was mixture of *erythro*-3-methyl-2-pentyl acetate and 2-octyl acetate. [e] Acetate conversion was in the 20–40% range. [f] Ratio in reactant feed was 7.81. [g] Acetate conversion was greater than 80%.

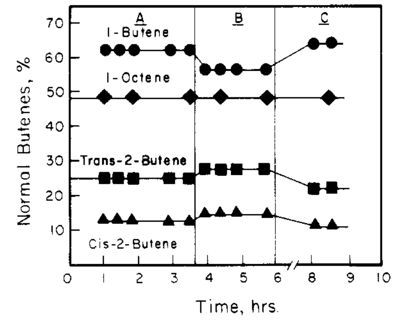

Figure 2. Normal butene distribution from the pyrolysis of undeuterated and 1,1,1-trideuterio-2-butyl acetate in 2-octyl acetate over high surface area (380 m^2/g) silica at 623 K (regions A and C refer to conversions with unlabeled butyl acetate and region B to conversion of deuterated butyl acetate).

propane plus 2-methylpropene. Thus, the butyl group decomposed to produce normal butenes, and the acetate group (or acetic acid) underwent secondary reactions to produce a variety of products. However, these products need not be considered in detail in the current study.

1,1,1-Trideuterio-2-butyl acetate was also pyrolyzed at 623 K over the high surface area silica (380 m^2/g). The products (Figure 2) show less of an isotope effect than was obtained with the glass beads; with the high area silica the kinetic isotope effect for the formation of the butenes was only 1.26. Again, the 2-butenes contained, within experimental error, three deuteriums, and the 1-butene contained two deuteriums.

d,l-erythro-2-Butyl-*3*-d_1 acetate was also pyrolyzed at 623 K when the reactor tube contained high surface area silica (380 m^2/g). The deuterium contents for the butene products were as follows: 1-butene, 96%; *trans*-2-butene, 97%; and *cis*-2-butene, not detectable (less than 0.1%) after correcting for the amount of d_0 in the butyl acetate reactant. Thus, the data show that greater than 98% of the elimination occurred by a syn mechanism. The product distributions (Tables I and II) for the labeled and unlabeled butyl acetate were 1-butene (65 and 61%), *trans*-2-butene (25 and 26%) and *cis*-2-butene (10 and 13%), respectively. These data correspond to a kinetic isotope effect of 1.3 for the alkene-forming step; since the amount of the *cis*-2-butene is small there is considerable error associated with the determination of this kinetic isotope effect.

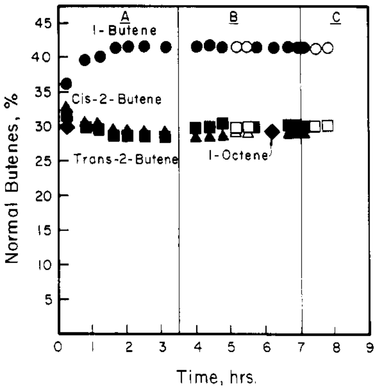

Figure 3. Alkene distribution from the dehydration of *d,l-erythro*-2-butanol-*3*-d_1 and unlabeled 2-butanol in 2-octanol (◇) over high surface silica (380 m^2/g), at 573 K (unfilled symbols) and at 623 K (filled symbols) (regions A and C refer to conversions with unlabeled butyl acetate and region B to conversion of deuterated butyl acetate).

d,l-erythro-2-Butyl-*3*-d_1 acetate was pyrolyzed over the 3-mm glass beads to produce an isotope effect of 1.78. Again, there is considerable error because the amount of the *cis*-2-butene is small. The deuterium content of the butenes indicate that greater than 98% of the elimination occurred by a syn mechanism.

The corresponding alcohol, *d,l-erythro*-2-butanol-*3*-d_1 (12 mol % in 2-octanol), was also converted at 573 or 623 K over the high surface area silica. As can be seen from the data in Figure 3, there was no measurable kinetic isotope effect for the conversion of 2-butanol at either temperature. The unlabeled alcohol was converted over the hydrogen pretreated silica for about 3.5 h, and then the flow of this reactant was terminated but a nitrogen flow was continued while the feed was switched to the labeled alcohol; this alcohol was then passed over the silica for

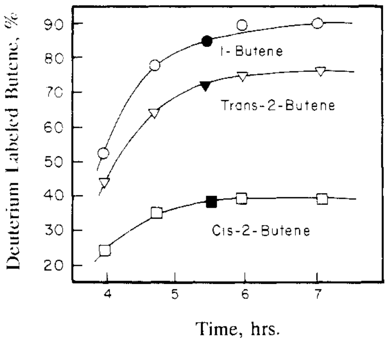

Figure 4. Deuterium content in the butene products for *erythro*-2-butanol-*3*-d_1 conversion over silica at 623 K (filled symbols) and at 573 K (unfilled symbols).

slightly more than 4 h, and then a nitrogen flow was continued while switching the feed back to the unlabeled alcohol. After the first 1.5 h the butene isomer distribution remained essentially constant for both the labeled and unlabeled feed. Furthermore, the octene isomers (1-, *cis*-2-, and *trans*-2-octene) followed the same trend; no change in the composition was noted when the feed was switched to or from the labeled alcohol. Unlike the conversion of the labeled acetate of this alcohol, where there was essentially complete loss of deuterium in the formation of the *cis*-2-butene and no deuterium loss in forming either the *cis*-2- or *trans*-2-butenes, a significant amount of labeled *cis*-2-butene was formed and both *trans*-2-butene and 1-butene lost significant amounts of deuterium. The deuterium content for the butenes increased with reaction time and appeared to attain a constant value at later reaction times (Figure 4). At the later reaction times (6–8 h) the amount of deuterium incorporated in *cis*-2-butene is about the same as the amount lost in forming 1- and *trans*-2-butene; obviously, this is not the case at earlier reaction times. Because of deuterium loss, the calculated amount of syn elimination appeared to increase with reaction time to attain a value of ca. 70% at later times on stream; this calculated value is low due to a deuterium scrambling reaction. Significantly, the deuterium content, and the calculated syn elimination percentage, did not appear to depend upon the reaction temperature. For the same reaction conditions at 623 K, there was not a detectable amount of alcohol dehydration in the presence of 3-mm glass beads.

Thus, the conversion of *d,l-erythro*-2-butanol-*3*-d_1 over the high surface silica differs from that of the corresponding acetate; the alcohol produces considerably smaller amounts of 1-butene and a correspondingly larger amount of *cis*-2-butene, and significant amounts of deuterium exchange had occurred in all three butene isomers. Note also, from the data in Figures 2 and 3, that 2-octyl acetate produced 49% 1-octene while 2-octanol produced 29% 1-octene; thus, the same trends are obtained for the C_4 and C_8 reactants.

A mixture of 1-butene and D_2O was passed over the high surface area silica at 623 K and a flow rate that was approximately the same as used in the pyrolysis runs with this silica. Under these conditions H–D exchange did not occur to a sufficient extent to incorporate sufficient deuterium to detect by the GC–MS analysis. The addition or loss of deuterium in the alkene does not occur through secondary reactions during alcohol dehydration; thus, the exchange must not occur following the alkene-forming step.

The pyrolysis of 3-methyl-2-pentyl acetate was carried out over the 3-mm glass beads at 623 and 673 K (Table II). The alkene layer was washed with water prior to analysis since a small amount of an unidentified pyrolysis product co-eluted with *cis*-3-methyl-2-pentene. For a mixture of equal amounts of threo and erythro isomers, the cis/trans ratio of the 3-methyl-2-butenes from pyrolysis at 623 K is 1.50. On the other hand, the cis/trans ratio is ca. 0.04 or less for the 3-methyl-2-butenes formed during the pyrolysis of the acetate of the pure erythro isomer. There is an appreciable amount (ca. 4%) of the cis alkene isomer in the initial sample for the pyrolysis of the erythro product; however, the percentage of *trans*-alkene is the same in all other samples. 1-Alkene isomerizes to produce the *cis*-alkene selectively;[9] hence, it appears that a secondary isomerization reaction converts 1-alkene to *cis*-2-alkene during the early stages of pyrolysis with the fresh glass beads.

Discussion

For conversions with the high surface area silica, the deuterium content and isomer distribution both show that alcohol and ester conversion occur by different reaction pathways. The butenes (and octenes) formed from the alcohol are near the equilibrium composition among the isomers permitted by β-elimination. Thus, the products from alcohol dehydration on high surface area silica are those expected if product stability determines the alkene distribution, as for example, in a carbonium ion like mechanism. Furthermore, the H–D exchange during alcohol dehydration, but not for water and butene, indicate that the exchange occurs during the dehydration step and not as a secondary reaction of primary products. This lack of isotope exchange as well as the high fraction of 1-butene in the butene products from butyl acetate pyrolysis are strong evidence that alcohol dehydration and acetate pyrolysis do not occur through a common intermediate. It also appears that dehydration over high surface area silica follows a reaction that involves a more ionic intermediate than pyrolysis does.

The absence of a measurable isotope effect in the dehydration of 2-butanol with a silica catalyst is surprising. However, we have found that there is at most a very small isotope effect for the dehydration of secondary and tertiary alcohols with several oxide catalysts.[10] Thus, the result for dehydration of alcohols with high surface area silica should not be viewed as unusual. The lower isotope effect for acetate pyrolysis at 623 K than at 573 K suggests that surface catalysis may become a consideration at the higher temperatures with the high surface area silica but not with the glass beads.

The deuterium isotope effect, k_H/k_D, is approximately 2 for a number of elimination reactions. For example, eliminations from alcohols in solution provide isotope effects that range from ca. 1.7 to 2.1; this includes solvents ranging from very polar (acetonitrile) to nonpolar (toluene) and a range of leaving groups (hydroxide, tosylate, and triphenylphosphine oxide).[11] For the most part, k_H/k_D is usually in the range of 2 to 3 for base-catalyzed alkene formation by elimination from alkyl halides,[12] although considerably higher values have been obtained for some

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(10) Dabbagh, H. A.; Davis, B. H., manuscript in preparation.

(11) Dabbagh, H. A.; Franzus, B.; Huang, T. T.-S.; Davis, B. H., Submitted to *J. Org. Chem.*

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(18) We have obtained data that indicates that deuterium exchange occurs during alcohol dehydration with a thoria catalyst; this raises questions about the mechanism advanced in ref 15.

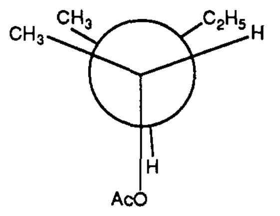
special bases or reactant substituents. The catalytic dehydration of alcohols is another widely studied reaction;[13-18] an isotope effect of ca. 2 is commonly obtained for this catalytic reaction. Thus, the isotope effect of 2.0 for pyrolysis of 2-butyl acetate in the presence of glass beads falls within the range of values normally encountered for eliminations in solution. However, a wide range of temperatures have been used in the above studies.

At 623 K the kinetic isotope expected is k_H/k_D ca. 2.6 for a difference in C-H and C-D of ca. 5.8 kJ/mol (2.88 and 2.46 at 573 and 673 K, respectively). Thus, apart from the 623 K data with the high surface area silica, the kinetic isotope values we obtained experimentally are not much lower than the theoretical values. However, the isotope effect at 623 K for the high surface area silica appears to be low. In addition, the butene distribution at 623 K with the high surface area silica is not in line with those obtained at other temperatures; the amount of the 1-isomer is higher than expected in view of the data obtained at higher and lower temperatures and with other silicas. The pyrolysis data differ from that of the alcohol dehydration and show that the butyl group leading to the butenes cannot be the same in the two reactions.

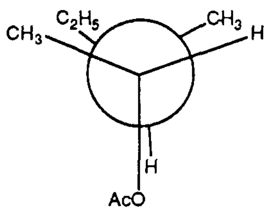
Noller and co-workers have studied the formation of butenes from deuterium-labeled 2-butanol and 2-butyl acetate using metal phosphate catalysts.[19,20] A microreactor was used in these studies so that successive pulses were injected into a carrier gas stream. Thus, these experiments were carried out so that the partial pressure of the acetate or alcohol was much lower than 1 atm; this provides conditions which permit competitive adsorption by the alkene products and may permit secondary reactions. For *d,l-erythro-* or *d,l-threo*-2-butyl-*3-d*$_1$ acetate pyrolysis, they found simultaneous syn and anti elimination; the extent of syn elimination ranged from 36 to 46 for $CaHPO_4$, $Ba_3(PO_4)_2$, $Ca_3(PO)_4)$, and $AlPO_4$ catalysts. All catalysts favored Saytzeff (2-butene) products. The deuterium isotope effect ranged from 1.3 to 2.2. On the other hand, syn elimination was observed for the dehydration of the corresponding alcohol with these catalysts. Our results cannot be reconciled with those obtained by Noller et al.[19,20]

One of the arguments presented to support a catalytic reaction pathway was based upon the products from the pyrolysis of 3-methyl-2-pentyl acetate.[21] The authors[8] stated that in the pyrolysis of 3-methyl-2-pentyl acetate the cis/trans ratio is two, while a ratio of one would be anticipated: "If only cis eliminations occur, then *cis*-3-methyl-2-pentene is formed from *threo*-3-methyl-2-pentyl acetate and *trans*-3-methyl-2-pentene is formed from *erythro*-3-methyl-2-pentyl acetate. This means that the 1-alkene/2-alkene ratio for the threo isomer is half that of the erythro isomer. Why is the 1-alkene/2-alkene ratio for two compounds as similar as *erythro-* and *threo*-3-methyl-2-pentyl acetate so different, when there is in general so little difference between the k_1^H/k_2^H ratios of the quite different compounds in Table II?"

A syn elimination for pyrolysis of 3-methyl-2-pentyl acetate should have the following structures: The methyl-ethyl interaction in the conformation for the erythro isomer should make this a higher energy transition state for a syn pyrolysis mechanism than the one for the threo isomer. The conformations leading to syn elimination from the two isomers to form 1-alkene will be mirror images and thus have the same reactivity. Hence, we expect different 1-alkene/2-alkene ratios for pyrolysis of threo and erythro acetates, and this is our experimental observation. The 1-alkene/2-alkene ratio for pyrolysis of the erythro isomer is 2.70 while the ratio from the mixture is 2.13. Assuming that the extent of pyrolysis to form 1-alkene is the same for both isomers permits us to calculate that the 1-alkene/2-alkene ratio produced from the pyrolysis of the threo isomer is 1.63. This leads, for an equal amount of 1-alkene formed from each isomer, to a *cis*-2-alkene/*trans*-2-alkene ratio of 22.7/13.0 = 1.74 for pyrolysis at 623 K. This means that the activation energy for a syn pyrolysis mechanism for the erythro acetate is 0.68 kcal/mol (2.86 kJ/mol) higher than for the anti pathway. Considering an energy of 4–8 kcal/mol (16–33 kJ/mol) for the energy difference between the staggered and the eclipsed conformation of butane, a difference of 0.68 kcal/mol is not unreasonable for the difference between structures I and II above. Thus, the product distributions, the 1-alkene/2-alkene ratio as well as the *cis*-2-alkene/*trans*-2-alkene ratio, from the pyrolysis appear reasonable and do not appear to require a steric requirement from a catalyst.



(threo, I)



(erythro, II)

In summary, the pyrolysis products from 3-methyl-2-pentyl acetate and from two deuterium-labeled butyl acetates are consistent with a simple pyrolysis mechanism that does not require a catalytic surface. High surface area silica was shown to have some catalytic activity for 2-butanol dehydration, but this material catalyzed at the same time hydrogen isotope exchange. High surface silica did not catalyze a measurable amount of exchange between D_2O and C_4H_8 under the conditions used for the alcohol dehydration. The higher kinetic isotope, and the lack of deuterium–hydrogen exchange when glass beads were used rather than the high surface area silica which did effect catalysis indicates that gas-phase pyrolysis greatly dominates over any catalytic effects of the glass beads (low surface area silica).

Experimental Section

Materials. 1,1,1-Trideuterio-2-butanol (TB) was prepared from the reaction of trideuteriomethylmagnesium iodide with propionaldehyde in ethyl ether; after proper workup TB was fractionally distilled at 98–99 °C to give 58% yield at greater than 99% purity (GLC). The deuterium (^2H NMR) analysis of the alcohol and the mass spectra of the butenes indicated at least 89% isotopic purity. *d,l-erythro*-3-Deuterio-2-butanol (EDB) was prepared from the reduction of *trans*-2,3-epoxybutane with $LiAlD_4$ in ethyl ether (bp 97–98 °C, 72% yield, 98 atom % D).

Esters were prepared from the reaction of an alcohol with acetic anhydride in the presence of pyridine; their physical properties were in agreement with literature values. Aerosils (50 and 380 m^2/g) were obtained from Degussa, Inc., and the glass beads (0.25 mm and 3 mm) were purchased from American Scientific Products. Surface areas were obtained using nitrogen adsorption and the BET equation. All starting materials were obtained from Aldrich Chemical Co.

Pyrolysis Procedure. A glass plug flow reactor was filled with silica or glass beads, heated at 450 °C in flowing hydrogen for 5–10 h, and then flushed for several hours with nitrogen. The

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esters were added at the top of the reactor at 1.2 cm^3/h (reactor volume ca. 30 cm^3), without a carrier gas flow. Products were collected in a trap maintained at dry ice temperature.

Product Analysis. Total conversion and the composition of the products were determined by GC using 30 m × 3.2 mm column packed with 23% SP-1700 on 80–100-mesh Chromosorb AAW and DB5 (60 m × 0.25 mm). The deuterium content of each butene isomer was determined using a HP5985A GC mass spectrometer equipped with a 30 m × 0.53 mm bonded Alteck FSOT RSL-160 capillary column and operated at 10 eV. The isotope composition of butenes were calculated from the area of *m/e* 56 and *m/e* 57. Peak *m/e* (M − 1) was very small (<2%); thus, the contribution of (M − 1) peak (*m/e* 56) for C_4H_7D should likewise be small so that it can be ignored. The deuterium isotope effect was calculated using the relative weight percent butenes from graphs 1 and 2 in the following equations:

$$\frac{k_h}{k_d} = \frac{(\text{1-butene})_H/(cis\text{-2-butene} + trans\text{-2-butene})_H}{(\text{1-butene})_D/(cis\text{-2-butene} + trans\text{-2-butene})_D}$$

for 1,1,1-trideuteriobutyl acetate and

$$\frac{k_h}{k_d} = \frac{(cis\text{-2-butene})_H/(trans\text{-2-butene} + \text{1-butene})_H}{(cis\text{-2-butene})_D/(trans\text{-2-butene} + \text{1-butene})_D}$$

for *d,l-erythro*-2-butyl-3-d_1 acetate.

Registry No. TB, 53716-61-3; EDB, 10277-59-5; SiO_2, 7631-86-9; tri-deuteriomethyl iodide, 865-50-9; propionaldehyde, 123-38-6; deuterium, 7782-39-0; *trans*-2,3-epoxybutane, 21490-63-1; 3-methyl-2-pentyl acetate, 34860-03-2; *erythro*-3-methyl-2-pentyl acetate, 24512-83-2; 2-octyl acetate, 2051-50-5; sec-butyl acetate, 105-46-4.

Regiospecific and Chemoselective Ring Opening of Epoxides with Trimethylsilyl Cyanide–Potassium Cyanide/18-Crown-6 Complex[1]

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Trimethylsilyl cyanide with catalytic potassium cyanide/18-crown-6 complex opens epoxides regiospecifically to give 3-((trimethylsilyl)oxy) nitriles. The addition of cyanide occurs at the least substituted carbon. The reaction is chemoselective for monosubstituted epoxides due the participation of a pentavalent silicon species.

Introduction

Ring-opening reactions of epoxides with trimethylsilyl cyanide under Lewis acid catalysis have been the subject of considerable interest over the last 15 years. Trimethylsilyl cyanide is well known to exist in equilibrium with its isocyanide,[2] and due to this ambident nature, one may, by judicious choice of an appropriate catalyst, selectively obtain either β-((trimethylsilyl)oxy) nitriles[3] or isonitriles.[4] In general, harder Lewis acids (i.e., those containing aluminum) favor the formation of nitriles, while softer ones (containing zinc, tin, gallium, and palladium) favor isonitriles.[5] Control over the ambident nucleophilicity of trimethylsilyl cyanide as a function of the Lewis acid employed has been rationalized in terms of HSAB theory.[4b]

Regioselectivity in the formation of isonitriles invariably gives nucleophilic addition at the most highly substituted carbon,[6] suggesting that coordination of the Lewis acid to the epoxide oxygen and commensurate bond stretching toward a carbocation-like intermediate precedes nucleophilic attack. Attempts to delineate the course of regioselectivity in nitrile formation, however, have given conflicting results. Lidy and Sundermeyer found the cyano group added to the *most* highly substituted carbon in the reaction of trimethylsilyl cyanide with 2,2-dimethyloxirane and catalytic aluminum chloride.[3a] Mullis and Weber, on the other hand, reported that the same substrate underwent ring cleavage to give the cyano group at the *least* substituted carbon with either aluminum chloride or diethylaluminum chloride catalysis.[3b] Imi, Yanagihara, and Utimoto, also using 2,2-dimethyloxirane, obtained a mixture of nitrile (substitution at C-1), isonitrile (substitution at C-2), and a rearranged product with catalytic diethylaluminum chloride.[5] In their study, the isonitrile predominated. This group has also studied the effects of various Lewis acid catalysts, both hard and soft, on regioselectivity and on the ambident character of trimethylsilyl cyanide.[5]

Investigations of *anionically* catalyzed ring opening of epoxides with trimethylsilyl cyanide have, up to now, been left unexplored, although related carbonyl insertion reactions were studied by Evans as early as 1973.[7] Strong nucleophiles are well known to attack epoxides at the site offering the least steric hindrance. Thus, unambiguous ring opening to obtain regiochemically pure nitrile products by the use of an appropriate anionic catalyst was anticipated at the onset of this study. Our results, using potassium cyanide/18-crown-6 complex[7b] are described below. In addition to the expected regiospecific ring openings, under the conditions employed, we observed selective

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[6] The exception to this is propylene oxide, which gives ~1:1 mixtures of regioisomers with $Pd(CN)_2$, $SnCl_2$, and Me_3Ga (see ref 5).

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