

washed twice with ether and recrystallized from acetone to give colorless crystals of 3-piperidino-2-(α,α -dideuteriobenzyl)-1-indanone hydrochloride (VIIa), m.p. 210° dec.

Anal. Calcd. for $C_{21}H_{22}D_2NOCl$: C, 73.34; H, 7.10; N, 4.07; Cl, 10.31. Found: C, 73.30; H, 6.96; N, 4.07; Cl, 10.46.

The hydrogen analysis accounts for 6.45% hydrogen and 1.17% deuterium such that the calculated percentage of hydrogen as obtained by a routine analysis is 7.10%.

The proton magnetic resonance spectrum of 3-piperidino-2-(α,α -dideuteriobenzyl)-1-indanone (VIa), as derived from the above hydrochloride, shows nine aromatic protons in the range 2.0–3.0 τ and two protons splitting each other with a $J_{ax} = 3$ c.p.s. at 5.86 τ for the proton on the same carbon as the piperidino group and at 7.04 τ for the proton on the same carbon as the α,α -dideuteriobenzyl group. The signals from the protons of the

piperidino group occur as two broad peaks, one corresponding to four protons at 7.82 τ and one corresponding to six protons at 8.63 τ (Fig. 1).

(c) **With Piperidine in Benzene.**—A solution of 0.30 g. of IVa and 1.00 g. of piperidine in 40 ml. of benzene was maintained at 90° for 60 hr. A precipitate of 0.13 g. of piperidine hydrobromide (80% yield) was filtered off. The solution was evaporated under reduced pressure to give an oil. The proton magnetic resonance spectrum indicated that the oil contained 46% of 2-(α,α -dideuteriobenzyl)-1-indanone (Va) and 43% of 3-piperidino-2-(α,α -dideuteriobenzyl)-1-indanone (VIa).

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Pyrolysis of *sec*-Butyl Acetate. Stereospecific *cis* Elimination¹

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The acetates of *d,l*-threo- and *d,l*-erythro-3-deuterio-2-butanol were pyrolyzed at 400°. Both *cis*- and *trans*-2-butenes were formed in stereospecific *cis* eliminations.

The cyclic intramolecular mechanism for the pyrolyses of esters having β -H, as first proposed by Hurd and Blunck,² has been generally accepted. The strongest evidence in support of the mechanism for this vapor phase decomposition as well as those of amine oxides,^{3a} xanthates,^{3b} and chloroformates⁴ has resulted from stereochemical studies.⁵ In all cases the predominant olefinic products are the result of the expected *cis* eliminations. However, there are produced during the acetate pyrolyses differing amounts of olefins which are not the result of *cis* eliminations. When *cis*-2-methylcyclohexyl acetate was decomposed in the vapor phase at 500°, Arnold, Smith, and Dodson⁶ found 1-methylcyclohexene as 25% of the olefinic products. Alexander and Mudrak⁷ found 7.2% 1-phenylcyclohexene in the olefins produced when *cis*-2-phenylcyclohexyl acetate was pyrolyzed at 600°. Similar results were obtained when Curtin and Kellom⁸ studied the stereochemistry of pyrolytic elimination in an acyclic system. The acetate of *d,l*-threo-2-deuterio-1,2-diphenylethanol was pyrolyzed at 400° and the resulting *trans*-stilbene was 26% monodeuterated. In all these studies significant amounts of olefins were produced which did not result from a *cis* elimination. The cyclic intramolecular mechanism is not compatible with these products and a second reaction path must be operating if these are the primary products. Since it is not clear that the earlier studies excluded the possibility that the primary products were not stable under the reaction conditions, the *sec*-butyl system was investigated with the expectation of avoiding this difficulty.

(1) This research was sponsored by the U. S. Army Research Office (Durham).

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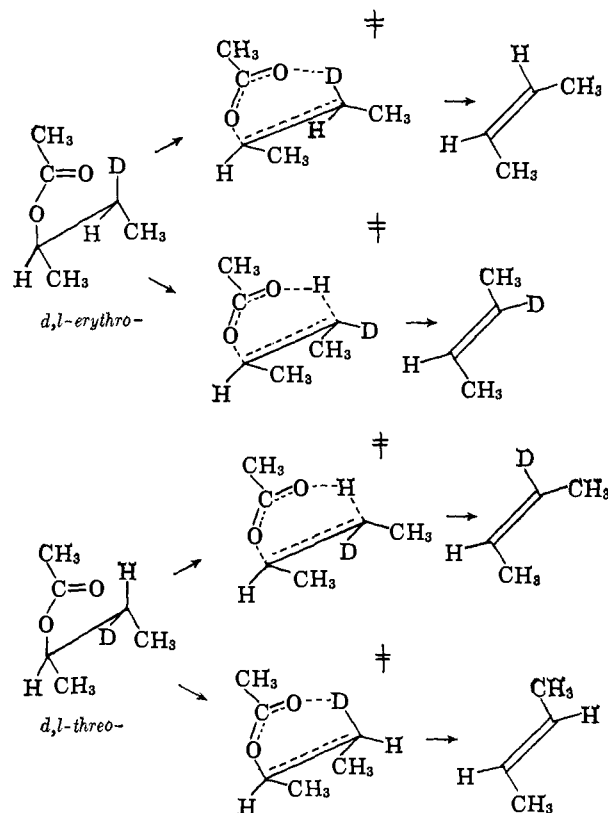
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The acetates of *d,l*-erythro- and *d,l*-threo-3-deuterio-2-butanol were pyrolyzed at 400° to investigate the stereochemistry of elimination in the *sec*-butyl system. The products expected *via* a cyclic transition state are shown in the reaction schemes.



The butenes produced were analyzed, separated, and purified by vapor phase chromatography. The individual fractions were then analyzed by mass spectrometry at low voltages. The heights of the parent peaks for masses 56 and 57 were taken as a measure of the relative amounts of undeuterated and

monodeuterated butene in the sample. The results are given in Table I.

TABLE I
PYROLYSIS OF *sec*-BUTYL ACETATE AT 400°

Acetate isomer	—Olefin composition, %—			Monodeuterated, %	
	1-Butene	<i>trans</i> -2-Butene	<i>cis</i> -2-Butene	<i>cis</i> -2-Butene	<i>trans</i> -2-Butene
<i>d,l</i> - <i>erythro</i>	61	30	9	3	97
<i>d,l</i> - <i>threo</i>	63	19	18	94	4
Undeuterated	57	28	15

To establish the purity of the acetates, the alcohols from which the acetates were prepared were also converted to the corresponding tosylates. The tosylates were then subjected to base elimination (E2) conditions and the resulting butenes were analyzed in the same manner as the pyrolyses products. The results of these analyses are given in Table II.

TABLE II
BASE ELIMINATION OF *sec*-BUTYL TOSYLATES

Tosylate isomer	—Olefin composition, %—			Monodeuterated, %	
	1-Butene	<i>trans</i> -2-Butene	<i>cis</i> -2-Butene	<i>cis</i> -2-Butene	<i>trans</i> -2-Butene
<i>d,l</i> - <i>erythro</i>	55	26	19	95	2.6
<i>d,l</i> - <i>threo</i>	50	13	37	4	97
Undeuterated	48	33	19

These values serve as standards for the acetate pyrolyses and are internally consistent with previous findings of a *trans* ring opening in the reduction of epoxides by LiAlH_4^9 and a *trans*-E2 elimination. Thus, the conformational and isotopic purity of the alcohols was at least 95%.

By comparing the butene products from both the pyrolytic and E2 elimination reactions the extents of *cis* elimination in the formation of the 2-butenes from the acetate pyrolyses were calculated and the results are given in Table III.

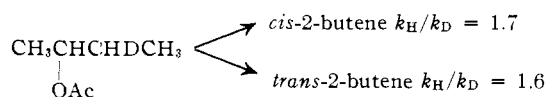
TABLE III
PERCENTAGE OF OLEFINS PRODUCED BY A *cis* ELIMINATION DURING ACETATE PYROLYSIS

Acetate isomer	Butene formed by <i>cis</i> elimination, %	
	<i>cis</i> -2-Butene	<i>trans</i> -2-Butene
<i>d,l</i> - <i>erythro</i>	$97/97 \times 100 = 100 \pm 3$	$97/95 \times 100 = 102 \pm 3$
<i>d,l</i> - <i>threo</i>	$94/97 \times 100 = 97 \pm 3$	$96/96 \times 100 = 100 \pm 3$

It is evident that within experimental limits the pyrolyses products are the results of stereospecific *cis* eliminations. All the products can be explained by the mechanism involving a cyclic intramolecular transition state. Since in the reported instances of non-*cis* elimination the stability of the primary products was not established, it is reasonable to suppose for the present that the lack of stereospecificity observed was attributable to isomerization processes.

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It is possible to calculate the isotope effects in the formation of *cis*- and *trans*-2-butenes with the assumption that the rate of 1-butene production is not affected by D substitution in the 3-position.



Isotope effects for acetate pyrolyses derived from absolute rate measurements fall between 1.7 and 2.8.⁵ The isotope effects for the *cis* elimination in *sec*-butyl chloroformates are 1.4 and 1.3 for the formation of *cis*- and *trans*-2-butenes, respectively.⁴

Experimental

***d,l*-erythro-3-Deuterio-2-butanol.**—By the reduction of *trans*-2,3-epoxybutane with LiAlD_4 using the procedure of Helmkamp,¹⁰ this alcohol was prepared in a 62% yield, b.p. 97.7°, n_D^{25} 1.3948.

***d,l*-threo-3-Deuterio-2-butanol.**—From *cis*-2,2-epoxybutane this alcohol was prepared in a 38% yield, b.p. 97.6°, n_D^{25} 1.3948.

Tosylates of Butanols.—The procedure of Tipson¹¹ was used to prepare the tosylates of the undeuterated and monodeuterated alcohols. The crude products isolated by the extraction, washing, and isolation technique of Brown and Nakagawa¹² were used without further purification.

Acetates of Butanols.—The acetates were prepared by treating the alcohols with acetic anhydride in the presence of fused sodium acetate. The purity of the deuterated acetates was found to be greater than 95% by vapor phase chromatography using a 0.75% fluorosilicone column. The crude deuterated acetates had the same refractive indices, n_D^{25} 1.3869.

Pyrolysis of Acetates at 400°.—The undeuterated and deuterated acetates were pyrolyzed in a 10 × 200 mm. vertically mounted pyrolysis tube packed with 1/8 in. glass helices. The tube was placed in a furnace and heated to 400 ± 5°. The acetates were added at the top of the tube. During this period a helium stream of 5 to 10 ml. per min. was passed through the tube. The products were collected in a Dry Ice-acetone trap attached to the bottom of the tube. The gaseous products after distillation through a -76° trap in a vacuum line represented a 31% yield from the *erythro*-acetate, a 37% yield from the *threo*-acetate, and a 61% yield from *sec*-butyl acetate. The butene products were analyzed, separated, and purified by vapor phase chromatography using a 23 ft. β,β' -oxydipropionitrile column at 0°. The results of these analyses are given in Table I. The mass spectrum analyses were performed on a Bendix 14-101 time-of-flight instrument to disclose the amounts of mono- and undeuterated butenes in each fraction.

Base Elimination (E2) of Tosylates.—In a 50-ml. three-necked flask fitted with a water condenser, magnetic stirrer, and a puncture-sealing vaccine bottle cap an ethanolic potassium ethoxide solution (25 ml., 1 M) was prepared from ethanol and potassium under a nitrogen atmosphere and taken to reflux. While a slow stream of nitrogen was passing through the system, the tosylate (0.7 g., 3 mmoles) was added dropwise over a 3-min. period. The butene products were collected in a liquid nitrogen-cooled trap attached to the top of the water condenser for 10 min. following the addition. The gaseous products were handled by the techniques described for the pyrolysis products. The *erythro*-tosylate was converted to butenes in a 58% yield and the yields from the *threo*- and undeuterated tosylates were 54 and 55%, respectively.

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