other hand, comparison of $\Delta H°$ for isomers **7** and **8** with isomers **12** and **13** reveals that methyl substitution at C-1 produces no reduction in H bond energy. Even for isomers **14** and **15**, the $\Delta H°$ values are equivalent within experimental error. The equivalency of $\Delta H°$ for compounds **7** and **14** indicates that the methyl group at C-7 syn to the hydroxyl at exo C-2 exercises no major steric effect upon the H bond strength.

The thermodynamic results for compounds **19** and **22** are not to be trusted since severe peak overlap occurred above 120°; consequently, the $K_X{}^*$ values are not to be trusted above this temperature, as well. (The $K_X{}^*$ values in Table IV are at 115° for these compounds.)

D. Pure Base Approach. In this method, the heats of solution of the alcohol and its corresponding ether were measured in the pure phosphate and the pure dotriacontane columns. The H bond enthalpy, $\Delta H°$, was then calculated by eq 10.

The values of $\Delta H°$ calculated by the pure base approach were found to be consistently lower (*ca.* 1–1.5 kcal/mole) than the values derived from the previous glc method. The low values undoubtedly result from lack of achievement of 100% complexation of the alcohol with TBPP. There are two reasons which would account for this: (1) the chromatographic temperatures are too high and (2) the pure phosphate is so highly associated that the few phosphoryl groups are available for H bonding. This, it appears that the pure base method cannot be used as a gas–liquid chromatographic technique for measuring H bond enthalpies at the temperatures used in this work.

Conclusion

Glc has been shown to be a worthwhile method for studying H bond complexes. The advantages of the method are: (1) measurements are made at infinite dilution of the solute so that self-association is not a problem; (2) purification is not required; and (3) the method is simple and rapid. As pointed out in the paper the disadvantages are: (1) secondary solvent effects can arise and (2) the precision in $\Delta H°$ is less than in calorimetry (however, comparable to other methods for determining $\Delta H°$). This study along with other recent ones[20] indicates that glc can become a standard method for studying reversible complexes.

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Mechanisms of Elimination Reactions. XVIII. The Effect of Base, Solvent, and Structure on Product Ratios in E2 Reactions of Some Sulfonium Salts[1]

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Abstract: The effect of changing from an *n*- to a *sec*- to a *tert*-butoxide–butyl alcohol medium on the products of the E2 reaction of 2- and 3-pentyldimethylsulfonium bromide was studied. For the 2-pentyl salt, the proportion of 1-pentene, the Hofmann rule olefin, increases from *n*- to *sec*-butoxide–butyl alcohol but decreases from *sec*- to *tert*-butoxide–butyl alcohol. The trans:cis ratio goes down at first, then sharply up, during the same changes. For the 3-pentyl salt, the trans:cis ratio shows the same behavior. The behavior on the change from *n*- to *sec*-butoxide–butyl alcohol is attributed to the change in the strength and bulk of the base. The reversal of this trend on the change from *sec*- to *tert*-butoxide–butyl alcohol was unexpected. A change of mechanism, perhaps to an α',β syn elimination, may be responsible. The reactions of 4-methyl-2-pentyl- and 2-methyl-3-pentyldimethylsulfonium bromide with *n*- and *sec*-butoxide–butyl alcohol were also studied. In both cases, there was an increase in the proportion of the Hofmann rule olefin accompanied by an increase in the trans:cis ratio. This pattern was previously observed with quaternary ammonium salts, and suggests the incursion of syn elimination at the *sec*-butoxide–butyl alcohol stage with these more highly branched reactants.

In E2 reactions, the change to stronger bases is expected to increase the reactant-like nature of the transition state (*i.e.*, decrease the double bond character).[4] This change can be effected by increasing the branching of an alkoxide base which, in addition, would also increase any steric interactions.[5] Both factors would favor formation of a less alkylated (Hofmann rule) olefin.

For a purely anti elimination, any change in reaction conditions that results in a transition state with less double bond character, such as an increase in base strength, should increase the proportion of the thermodynamically less stable cis olefin at the expense of the trans olefin. Increasing the steric requirements of the

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(2) Chas. Pfizer Fellow, 1967–1968.

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base also favors the formation of the cis olefin.[6,7] In an anti elimination of a substrate capable of producing both positional and geometrical isomers, then, a more highly branched alkoxide base will cause an increase in the proportion of the Hofmann rule olefin accompanied by a decrease in the trans:cis ratio. This is indeed the case for E2 reactions of alkyl halides[5,8-10] and tosylates[6,10-12] and is called the "normal" pattern.[12,13] In support of this conclusion, it is known that syn elimination is only a minor pathway in the formation of 5-decene from 5-decyl tosylate, even with *tert*-butoxide ion in *tert*-butyl alcohol.[14]

When syn elimination competes with anti elimination[15] the increase in the reactant-like nature and/or the steric requirements of the transition state, caused by a more highly branched alkoxide base, will favor formation of the trans olefin by increasing the proportion of reaction that occurs through a syn pathway.[7,16] Now, the increase in the proportion of the Hofmann rule olefin will be accompanied by an increase in the trans:cis ratio, a situation known as the "abnormal" pattern.[13] The trend toward increasing Hofmann rule olefin with more highly branched base–solvent systems is not expected to be reversed by any accompanying increase in syn elimination. If anything, the trend should be enhanced.[13]

The "abnormal" pattern was observed for reactions of acyclic quaternary ammonium salts.[13] This was the pattern expected since acyclic quaternary ammonium salts are known to react increasingly through a syn pathway as the base becomes increasingly branched.[7]

We decided to test the generality of these different orientation patterns by studying the products from E2 reactions of substrates with a charged leaving group more reactive than the trimethylammonio group. Toward this end, 2-pentyl-, 3-pentyl-, 4-methyl-2-pentyl-, and 2-methyl-3-pentyldimethylsulfonium bromides were prepared and subjected to E2 reactions under a variety of conditions.

Results and Discussion

The results of reactions with 2- and 3-pentyldimethylsulfonium bromides are given in Tables I and II. For the 2-pentyl salt, the change from *n*-butoxide–*n*-butyl alcohol to *sec*-butoxide–*sec*-butyl alcohol caused an increase in the proportion of 1-pentene (the Hofmann rule olefin). The same change in the reaction conditions caused a decrease in the trans:cis 2-pentene ratio for both the 2- and 3-pentyl salts. In addition, a regular decrease in the trans:cis 2-pentene ratio was observed when the conditions to which the 3-pentyl salt was subjected were expanded to include the series hydroxide–water, methoxide–methyl alcohol, and ethoxide–ethyl alcohol. The trends in the product proportions for both the 2- and the 3-pentyl salts were reversed when the reaction medium was *tert*-butoxide ion in *tert*-butyl alcohol. The trends in the product proportions observed on changing from the *n*- to the *sec*-butoxide–butyl alcohol system will be discussed first, followed by a discussion of the trends obtained on changing from the *sec*- to the *tert*-butoxide–butyl alcohol system.

Table I. Olefin Proportions for E2 Reactions of 2-Pentyldimethylsulfonium Bromide at 35° in Alcohol Solvents

Alcohol[a]	% 1-pentene[b,c]	Trans:cis 2-pentene[c]	% olefin[d] yield
n-Butyl	93.1 ± 0.1	0.64 ± 0.02	46
sec-Butyl	96.5 ± 0.1	0.37 ± 0.02	39
tert-Butyl	86.7 ± 0.1	3.47 ± 0.01	44

[a] The base is the corresponding alkoxide. The reaction time is 12–16 hr. [b] 1-Pentene plus 2-pentene = 100. [c] Average and average deviations of repeated runs. [d] Based on starting material.

Table II. Olefin Proportions for E2 Reactions of 3-Pentyldimethylsulfonium Bromide in Alcohol Solvents

Solvent[a]	Temp, °C	Trans:cis 2-pentene[b]
Water	85	1.09 ± 0.02
Methyl alcohol	85	0.94 ± 0.02
Ethyl alcohol	85	0.84 ± 0.03
n-Butyl alcohol	35	0.71 ± 0.01
sec-Butyl alcohol	35	0.63 ± 0.02
tert-Butyl alcohol	35	5.00 ± 0.41

[a] The base is the conjugate base of the solvent. The reaction time is 120 hr. [b] The average and average deviation are given.

The trend to more Hofmann rule olefin and a lower trans:cis ratio, the "normal" pattern, observed on changing the reaction medium from *n*-butoxide ion in *n*-butyl alcohol to *sec*-butoxide ion in *sec*-butyl alcohol (Tables I and II) is the same as that observed for E2 reactions of the corresponding halides and tosylates (see above). The solvent effect is expected to be different for reactions involving leaving groups of different charge types.[17] The same trend for reactions of halides and tosylates on the one hand and sulfonium salts on the other suggests that the effect of changing the base–solvent system on product ratios is due to the change in the base. This same conclusion was drawn for reactions of quaternary ammonium salts.[13]

The increase in the proportion of 1-pentene when 2-pentyltrimethylammonium bromide was treated with increasingly branched base–solvent systems was attributed to an increase in the reactant-like nature of the transition state (*i.e.*, a decrease in double bond character) caused by an increase in the strength of the base.[13] A similar explanation for the sulfonium salts seems reasonable, although a steric effect cannot be ruled out.

A decrease in double bond character cannot alone be responsible for the decrease in trans:cis ratio from the *n*- to *sec*-alkoxides, for the ratios go well below unity. Such ratios for quaternary ammonium salts have been explained by Bailey and Saunders[7] as due to greater steric hindrance to proton abstraction in the transition state

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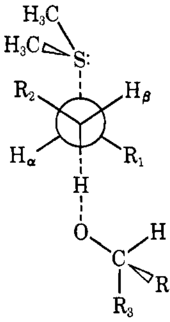
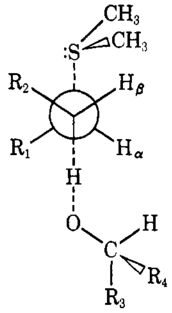
leading to trans rather than cis olefin. Whether the explanation can be applied to sulfonium salts, however, is uncertain, for the leaving group is smaller and unsymmetrical, and therefore not so effective in enforcing the conformations that produce the hindrance.

Another possible set of steric interactions is shown in **1** and **2**, where the base is placed so as to avoid R_2. In **1**, the methyl groups on sulfur must interact with either R_1 or R_2, while in **2** they can avoid both, so that **2** may be favored when eclipsing interactions between R_1 and R_2 are small. This model also helps to explain the fact that the trans:cis ratio runs higher for 3-pentyl than for 2-pentyl under the same conditions (compare Tables I and II). The group R_2 is larger for 2-pentyl than for pentyl (ethyl *vs.* methyl), and will lower the trans:cis ratio more for the former by favoring structure **2** in which methyl–R_2 interactions are avoided.

Syn elimination could also raise trans:cis ratios, and would be more important for a 3-pentyl than a 2-pentyl derivative. Enough syn elimination to produce the observed effect does not seem very likely, however, with *n*-butoxide or *sec*-butoxide as base.



1



2

The most remarkable feature of Tables I and II is the dramatic reversal of the product ratio trends for reactions in the *tert*-butoxide–*tert*-butyl alcohol system. The change from *sec*-butoxide–*sec*-butyl alcohol to *tert*-butoxide–*tert*-butyl alcohol caused a decrease in the proportion of 1-pentene and an increase in the trans:cis 2-pentene ratio for reactions of 2-pentyldimethylsulfonium bromide. Similarly, for reactions of 3-pentyldimethylsulfonium bromide, the change to the *tert*-butoxide–*tert*-butyl alcohol system caused an increase in the trans:cis 2-pentene ratio.

Taken at face value, these trends represent the "normal" pattern characteristic of anti elimination, since a decrease in Hofmann-rule olefin is accompanied by an increase in the trans:cis ratio. It has been suggested previously that the transition state for sulfonium salt eliminations is flatter and more product-like with *tert*-butoxide in *tert*-butyl alcohol than with ethoxide in ethanol because of a solvent effect,[18] and the present results are consistent with such an explanation. On the other hand, it is somewhat unsatisfying because it requires that the base strength be the controlling effect in the change from *n*-butyl to *sec*-butyl alcohol but that the solvent effect suddenly take over in the change from *sec*-butyl to *tert*-butyl alcohol. While such a reversal is possible, there is no ready rationale for it.

Another explanation for the unusual results with *tert*-butoxide in *tert*-butyl alcohol is that syn elimination is becoming important. The high trans:cis ratios can be readily explained in this way, but the decrease in Hofmann-rule product is the reverse of the trend expected from experience with quaternary ammonium salts.[7,13] A variant of the syn mechanism, the α′,β mechanism[19] must also be considered. Although it has been ruled out for the reaction of 2-phenylethyldimethylsulfonium ion with hydroxide ion in water,[20] it may be important with *tert*-butoxide in *tert*-butyl alcohol. There is no clear reason why an α′,β mechanism should give less Hofmann-rule product than a normal E2 reaction, though the attacking base is now a carbanion which may be less selective than an alkoxide. This does seem a less distasteful *ad hoc* assumption than that required if a more product-like transition state is assumed.[18]

Next, E2 reactions of sulfonium salts with more highly branched alkyl groups were examined. The olefin proportions obtained by treating 4-methyl-2-pentyl- and 2-methyl-3-pentyldimethylsulfonium bromides with *n*-butoxide ion in *n*-butyl alcohol and with *sec*-butoxide ion in *sec*-butyl alcohol are given in Tables III and IV. The reactions of the methylpentyl salts could not be studied in *tert*-butyl alcohol because of their insolubility.

Table III. Olefin Proportions for E2 Reactions of 4-Methyl-2-pentyldimethylsulfonium Bromide at 35° in Alcohol Solvents

Alcohol[a]	% 4-methyl-1-pentene[b]	Trans:cis 4-methyl-2-pentene
n-Butyl	96.5	1.46
sec-Butyl	97.8	2.84

[a] The base is the corresponding alkoxide. The reaction time is 12–21 hr. [b] 4-Methyl-1-pentene plus 4-methyl-2-pentene = 100.

Table IV. Olefin Proportions for E2 Reactions of 2-Methyl-3-pentyldimethylsulfonium Bromide at 35° in Alcohol Solvents

Alcohol[a]	% 4-methyl-2-pentene[b,c]	Trans:cis 4-methyl-2-pentene[c]	% methyl-alkyl ether[d]	% yield[e]
n-Butyl	75 ± 2	3.2 ± 0.5	92	90
sec-Butyl	85 ± 1	8.1 ± 0.5	88	70

[a] The base is the corresponding alkoxide. The reaction time is 58–84 hr. [b] 4-Methyl-2-pentene plus 2-methyl-2-pentene = 100. [c] Average deviation of repeated runs. [d] Determined by glpc with an internal standard. Ether + olefin = 100. [e] Total yield of ether and olefin determined by glpc with an internal standard.

Again, an increase in Hofmann-rule olefin is observed with the more branched *sec*-butoxide, but here the trans:cis ratios are greater than unity and *increase* when the medium changes from *n*-butoxide–*n*-butyl alcohol to *sec*-butoxide–*sec*-butyl alcohol. Eclipsing effects are expected to be larger in these more branched systems, and so is the tendency toward syn elimination.[7] In fact, the increase in Hofmann-rule olefin and trans:cis ratio is the "abnormal" pattern implying a competition between syn and anti elimination.

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Securing direct evidence for syn elimination from sulfonium salts is expected to be difficult, because the acidity of the α-hydrogens[21] leads to exchange,[21,22] and presumably also epimerization, at a rate comparable to or greater than that of elimination. It is still possible to test for the α',β mechanism by deuterium labeling,[20] and we hope to do that with reactants similar to those studied here. For the present, we must consider the normal E2, syn E2, and α',β mechanisms all to be possible contributors to sulfonium salt eliminations under various conditions.

Control experiments showed that the olefins formed were stable to more vigorous reaction conditions than used in the present study,[13] and that the E2 product proportions were not complicated by products formed from an E1 reaction. Thus, heating 2- and 3-pentyl- and 4-methyl-2-pentyldimethylsulfonium bromide in the same solvents and under the same conditions as were used for the E2 reactions, but with the alkoxide replaced by 2,6-lutidine, led to an undetectable amount of olefin. Heating 2-methyl-3-pentyldimethylsulfonium bromide in *n*-butyl alcohol in the presence of 2,6-lutidine, on the other hand, gave rise to a significant amount of olefin. The absence of a competing E1 process in the E2 reactions for this salt was proved by demonstrating the absence of a significant change in product proportions with changes in the initial base concentration in both *n*- and *sec*-butyl alcohol.[23]

Experimental Section[24]

2-Pentanol. A Grignard reaction of butyraldehyde (135 g, 1.9 mol), methyl iodide (140 ml, 2.3 mol), and magnesium turnings (61 g, 2.5 g-atoms) in 2 l. of anhydrous ether led to 92 g (55%) of 2-pentanol; bp 118–120°, n^{25}D 1.4030 (lit.[25] bp 119–119.5°, n^{20}D 1.4061). The purpose of using the Grignard reaction was to eliminate the possibility of the presence of 3-pentanol in commercial 2-pentanol.

2-Pentyl iodide was prepared in 47% yield by the dropwise addition of a solution of iodine (51 g, 0.2 mol) in dry dimethylformamide to an ice-cold stirred dimethylformamide solution of 2-pentanol (17 ml, 0.15 mol) and triphenylphosphine (50 g, 0.19 mol) under a nitrogen atmosphere according to the general method of Wiley, *et al.*[26] This method was chosen to elimination structural rearrangements that occur in other procedures.[27]

2-Pentylmethyl sulfide was prepared by treatment of 2-pentyl iodide (13 g, 0.07 mol) with sodium methanethiolate (0.14 mol) according to the method of Brown and Wheeler.[28] The product, in 42% yield, had bp 134–136° [lit.[28] bp 63–64° (60 mm)].

2-Pentyldimethylsulfonium bromide was prepared by allowing 2-pentylmethyl sulfide (3 g, 0.025 mol) and methyl bromide (20 g, 0.21 mol) to stand in 10 ml of dry acetonitrile in a sealed tube for 70 hr. After precipitation of the salt with excess anhydrous ether, several recrystallizations from ethanol–ether led to a 9% yield of white crystals, mp 125.5–128°. *Anal.* Calcd for $C_7H_{17}SBr$: C, 39.43; H, 8.05; S, 15.04. Found: C, 39.23; H, 7.97; S, 14.85.

3-Pentylmethyl Sulfide. Sodium (3 g, 0.14 g-atom) was dissolved in 200 ml of absolute ethyl alcohol. Methanethiol (5.5 ml, 0.1 mol) was added, and the solution was brought to reflux. 3-Pentyl tosylate,[12] dissolved in 150 ml of absolute ethyl alcohol plus enough anhydrous ether to effect solution, was added dropwise over a 2-hr period. After refluxing an additional 2 hr, the reaction mixture was cooled and added to 250 ml of water. The aqueous solution was extracted with petroleum ether (3 × 150 ml). The combined petroleum ether extracts were washed with water (3 × 100 ml) and dried over magnesium sulfate. Distillation through a Vigreux column gave 4.5 g (46% yield) of 3-pentylmethyl sulfide, bp 134–136°.

3-Pentyldimethylsulfonium bromide was prepared by treating 3-pentylmethyl sulfide (3 g, 0.025 mol) with methyl bromide (2 ml, 0.036 mol) in 10 ml of dry acetonitrile for 5 days at room temperature in a sealed tube. The salt was precipitated by adding the reaction mixture to excess anhydrous ether. 3-Pentyldimethylsulfonium bromide (5.1 g, 96%) had mp 130–133° dec. *Anal.* Calcd for $C_7H_{17}SBr$: C, 39.43; H, 8.05; S, 15.04. Found: C, 39.52; H, 7.95; S, 14.78.

4-Methyl-2-pentyldimethylsulfonium bromide was prepared in 15% overall yield from 4-methyl-2-pentyl tosylate[12] by the same procedure used to prepare 3-pentyldimethylsulfonium bromide (see above). The white crystalline salt had mp 162–163°. *Anal.* Calcd for $C_8H_{19}SBr$: C, 42.49; H, 8.43; S, 14.11. Found: C, 42.43; H, 8.35; S, 14.01.

2-Methyl-3-pentyl sulfide was prepared from 2-methyl-3-pentyl tosylate[12] by the same procedure used to prepare 3-penthylmethyl sulfide (see above). The clear liquid had bp 75° (90 mm). An analytical sample was purified by preparative gas chromatography. *Anal.* Calcd for $C_{17}H_{16}S$: C, 63.56; H, 12.19. Found: C, 63.67; H, 12.29.

2-Methyl-3-pentyldimethylsulfonium bromide was prepared by treatment of 2-methyl-3-pentylmethyl sulfide with methyl bromide in dry acetonitrile. The salt was extremely hygroscopic and, despite several attempts at purification, including repeated treatment with charcoal and precipitation from ethanol solution by ether, remained an oily, amorphous solid. It was dried in an Abderhalden apparatus and was used as such.

Procedure for Studies of Products from the E2 Reactions. The purification of the solvents and preparation of the alkoxide solutions were described previously.[12,13] Solutions of the alkoxide (0.1–0.8 *N*) and of the sulfonium salt (*ca.* 0.05 *N*) were equilibrated separately at the desired temperature, mixed together, and then returned to the bath. The work-up and glpc analysis were as previously described.[12,13]

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