

Steric Effects in Elimination Reactions. XI. The Reaction of Potassium *t*-Butoxide with 2-Butyl and *t*-Amyl Halides. The Effect of the Halogen on the Direction of Elimination¹

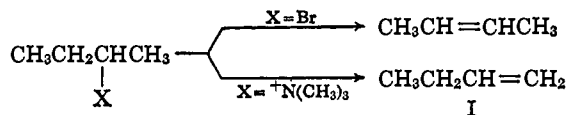
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Abstract. The reaction of the 2-butyl and *t*-amyl halides with potassium *t*-butoxide in *t*-butyl alcohol has been examined in order to establish the direction of elimination as a function of the halogen. The ratio of 1-olefin to 2-olefin increases in the order, chloride > bromide > iodide, in both series. The axial-equatorial equilibria of cyclohexyl compounds is proposed as a model for the steric interactions in the transition state for the E2 reaction. On this basis, the steric requirements of the halide leaving groups increase from iodide to bromide to chloride. These results in the halide series are consistent, therefore, with the previously suggested role of steric effects in shifting the direction of elimination from Saytzeff to Hofmann. It is pointed out that solvation, both of the attacking base and of the leaving group, must be considered in estimating their steric requirements and influence on the direction of elimination.

Directive effects in elimination reactions have been a source of considerable discussion in recent years.⁴ Hughes and Ingold and his co-workers pioneered in pointing out that the direction of bimolecular elimination appeared to follow two conflicting rules, the Saytzeff rule and the Hofmann rule.⁵

For example, bimolecular elimination of 2-butyl halides proceeds to give predominantly the more stable of the two possible olefins, 2-butene. On the other hand, elimination of 2-butyl -onium salts proceeds to give predominantly the less stable of the two possible olefins, 1-butene (I).



It was their proposal that elimination according to the Saytzeff rule in simple alkyl groups represented control of the elimination by electromeric stabilization of the double bond in the transition state. In other words, the reaction proceeds preferentially along a path leading to the more stable of the two possible products. This interpretation has been generally accepted and there appears to be no disagreement relative to it.

In the case of elimination according to the Hofmann rule, the reaction proceeds preferentially to the thermodynamically less stable of the two possible olefins. Obviously some new factor must be introduced by the -onium group which forces the reaction to proceed preferentially to form the energetically less favored product. Hughes and Ingold proposed that Hofmann rule eliminations represented control by the inductive factor, rendered important by the positive charge in the -onium ion.

(1) Based on a thesis submitted by Richard L. Klimisch in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Research assistant, 1961-1962, on a grant (G6273) supported by the National Science Foundation.

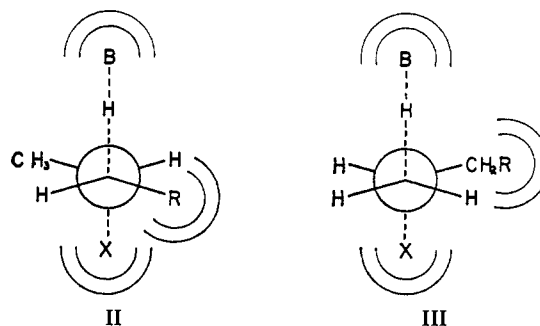
(3) X-R Fellow at Purdue University, 1962-1964.

(4) For a summary of the experimental data with a not unbiased interpretation of their implications, see J. F. Bunnett, *Angew. Chem. Intern. Ed. Engl.*, **1**, 225 (1962).

(5) M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw, and L. I. Woolf, *J. Chem. Soc.*, 2093 (1948).

In 1956 we suggested that the elimination according to the Hofmann rule represented dominant control by the steric factor.⁶

It is evident that in the usual bimolecular elimination of the type we are discussing, the direction of elimination will be determined by the relative stabilities of the two possible transition states leading to the two different olefins (II and III).⁷



In these transition states, there are evidently three centers where major changes in the steric requirements influencing the reaction could be achieved: (1) the attacking base B, (2) the alkyl group R on the incipient double bond of the 2-olefin; and (3) the leaving group X. It was our suggestion that in the absence of significant steric interactions, the reaction proceeds preferentially through transition state II, forming the more stable of the two possible olefins (Saytzeff rule). However, an increase in the steric requirements of the attacking base, or of the alkyl group on the incipient double bond, or of the leaving group, would result in larger steric interactions in transition state II than in III. Therefore such an increase should tend to shift the

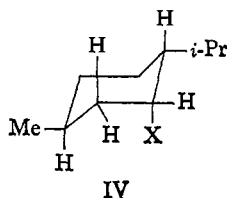
(6) (a) H. C. Brown, I. Moritani, and M. Nakagawa, *J. Am. Chem. Soc.*, **78**, 2190 (1956); (b) H. C. Brown, I. Moritani, and Y. Okamoto, *ibid.*, **78**, 2193 (1956); (c) H. C. Brown and M. Nakagawa, *ibid.*, **78**, 2197 (1956); (d) H. C. Brown and O. H. Wheeler, *ibid.*, **78**, 2199 (1956); (e) H. C. Brown and I. Moritani, *ibid.*, **78**, 2203 (1956).

(7) In this discussion we are assuming that the elimination in simple acyclic and monocyclic derivatives will proceed in a predominantly *trans* fashion: D. J. Cram in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 6. Moreover, for simplicity we are not distinguishing between the two different transition states (II-C and II-T) which lead to *cis*- and *trans*-2-olefins. Since both transition states arise from the same molecule, we need not concern ourselves with ground-state energies.

course of reaction from transition state II toward transition state III, *i.e.*, from Saytzeff toward Hofmann elimination.

This proposal was tested in a variety of systems and considerable data were accumulated; all were in agreement with the predictions of the proposed model.⁶

Indeed, in one instance the model served to correct an error in the literature which had been widely disseminated.⁵ Since cyclic derivatives are not free to rotate, such derivatives cannot relieve strains by achieving a transition state corresponding to III. Therefore, it is a consequence of the steric interpretation that the direction of elimination in molecules such as neomenthyl derivatives should be essentially independent of the steric requirements of the leaving group IV.



The elimination reactions of neomenthyl derivatives had been studied⁸ and it was pointed out by Ingold and his co-workers that the reported distributions, 75% 3-menthene from the chloride and 20% 3- from the trimethylammonium derivative, corresponded with the predictions of their theory. Clearly, this result was contrary to the predictions of the steric interpretation. However, a careful examination of the experimental part of Hückel's paper revealed that the actual distribution was 75% 3- and 80% 3- in the two cases—there had been an unfortunate error in entering the correct value in the proper column of the table. More recently Read has confirmed the predominant formation of the Saytzeff olefin in the elimination of the -onium salt.^{9,10}

The first experimental criticism of the steric theory was presented in 1960 by Saunders and his co-workers.¹¹ They measured the olefinic product distributions for a series of alkyl halides with potassium ethoxide in ethanol. These results are summarized in Table I.¹²

Table I. Per Cent of 1-Olefin in the E2 Reactions of 2-Pentyl and *t*-Amyl Halides with Potassium Ethoxide in Ethanol at 78°

Halogen, X	2-Pentyl X	<i>t</i> -Amyl X
Cl	37	43
Br	25	34
I	20	

(8) W. Hückel, W. Tappe, and G. Legutke, *Ann.*, **543**, 191 (1940).

(9) N. L. McNiven and J. Read, *J. Chem. Soc.*, 153 (1952).

(10) See E. D. Hughes and J. Wilby, *ibid.*, 4094 (1960), for a new explanation for this "anomalous" distribution in the bimolecular elimination of neomenthyltrimethylammonium ion.

(11) W. H. Saunders, Jr., S. R. Fahrenholtz, and J. P. Lowe, *Tetrahedron Letters*, No. 18, 1 (1960).

(12) The complete paper with more extensive data has recently appeared: W. H. Saunders, Jr., S. R. Fahrenholtz, E. A. Caress, J. P. Lowe, and M. Schreiber, *J. Am. Chem. Soc.*, **87**, 3501 (1965). In this paper the authors report their remarkable observation that 2-pentyl fluoride yields 82% 1-pentene and *t*-amyl fluoride yields 71% 2-methyl-1-butene. This result is clearly counter to the generalizations made by Hughes and Ingold and their co-workers⁸ and appears difficult to accommodate within the framework of the steric theory, unless solvation of the incipient fluoride ion in the transition state is exceedingly important. This point is discussed later in this paper. However, it should be pointed out that the reaction possesses some highly unusual features. Thus, the elimination reaction for 2-pentyl fluoride required "several

It was stated that "these results are obviously inconsistent with any reasonable formulation of the steric explanation."¹¹

Similarly, in his review,⁴ Bunnett states that these results are "contrary to H. C. Brown's hypothesis that a larger X group favors Hofmann elimination."

As it happens, our proposed interpretation is based on the *steric requirements* of the groups associated with the reaction center. The term *steric requirements* is not synonymous with *size*.

We had hoped that our extensive investigations of steric effects with the aid of molecular addition compounds had made it clear that mere size should not be equated with steric requirements. For example, there is no doubt that the size, *i.e.*, the total volume, of the groups, H, methyl, ethyl, and isopropyl, increases by large regular increments. However, the heats of reaction of boron trifluoride with pyridine, 2-methyl-, 2-ethyl-, and 2-isopropylpyridine reveal a large increase in strain in the first pair, but little change thereafter. Evidently the ethyl and isopropyl groups can rotate in such a manner that their steric requirements at the reaction site are only a little greater than those of methyl.¹³

There is no question but that the sizes of the halogens, as measured by the van der Waals' radii, increase from chlorine (1.8 Å), to bromine (2.0 Å), to iodine (2.2 Å). However, the covalent bond radii also increase: chloride (0.99 Å), bromine (1.14 Å), iodine (1.33 Å).¹⁴ As was pointed out earlier^{6d} the longer covalent radius of a heavier halogen may well compensate for the increased van der Waals radius, and both factors must be considered in estimating the steric requirements.

The confusion which apparently exists on this point suggested the desirability of returning to a study of the E2 eliminations of a family of related secondary and tertiary halides and of searching for some independent method for estimating the steric requirements of these halogens.

Results

The 2-butyl halides were selected as a representative secondary series for this study, rather than the 2-pentyl derivatives, because of the difficulties involved in preparing the latter compounds free of the 3-pentyl isomers.¹⁵ The *t*-amyl halides were adopted as a representative tertiary series. The *t*-butoxide-*t*-butyl alcohol system was selected because both the higher base strength of *t*-butoxide relative to ethoxide and the lower ionizing power of *t*-butyl alcohol relative to ethanol favors the E2 reaction over undesirable side reactions.¹⁶

days" in a sealed tube at 120° with an unspecified yield of olefin. Even the tertiary fluoride gave yields of only 7 to 15% of olefin in 13 to 104 hr at 120° with 1.2 M ethoxide. Nothing is known about the stereochemical aspects of the elimination of fluoride. This observation clearly is a highly important and interesting result. However, it appears desirable that the kinetics and mechanism for this reaction of alkyl fluorides be established as clearly E2 before one attempts to incorporate it within either of the competing interpretations. Unfortunately, the experimental phase of the present investigation had been completed prior to the time we learned of this important development.

(13) H. C. Brown, *J. Chem. Educ.*, **36**, 424 (1959).

(14) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(15) H. Pines, A. Rudin, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **74**, 4063 (1952).

(16) H. C. Brown and I. Moritani, *ibid.*, **76**, 455 (1954).

In order to minimize the effects of a concurrent E1 reaction, the base was used in large excess (1.0 *M*) to the halide (0.1 *M*). Tests revealed that the first-order reaction was unimportant for all of the secondary derivatives. In the case of the tertiary derivatives, the E1 component was <1% for the chloride, 7% for the bromide (6% previously noted¹⁵), and 25% for the iodide. These first-order contributions were subtracted graphically from the over-all reaction in order to obtain the product distribution for the pure E2 reactions. The results are summarized in Table II.

Table II. Olefin Distributions in the E2 Reactions of 2-Butyl and *t*-Amyl Halides with *t*-Butoxide in *t*-Butyl Alcohol at 50°

Halide	1-, ^a %	<i>trans</i> - 2-, ^b %	<i>cis</i> - 2-, %	Ratio of 1/2	Ratio of <i>cis</i> / <i>trans</i>
2-Butyl chloride	67	18	14	2.1	0.78
2-Butyl bromide	54	27.6	18.8	1.2	0.68
2-Butyl iodide	34	47.5	21.9	0.51	0.49
<i>t</i> -Amyl chloride	78	22		3.5	
<i>t</i> -Amyl bromide	73 ^c	27		2.7	
<i>t</i> -Amyl iodide	60 ^c	40		1.5	

^a 1-Butene or 2-methyl-1-butene. ^b *trans*-2-Butene or 2-methyl-2-butene. ^c Corrected for the accompanying E1 component.

The rate constants for the E2 reaction of potassium *t*-butoxide, 1.0 *M*, with *t*-amyl halides, 1.0 *M*, had been determined previously¹⁶ ($k_2 \times 10^5$, l. mole⁻¹ sec⁻¹): chloride, 0.00583; bromide, 0.338; iodide, 2.34.

Discussion

Our earlier results for the reaction of *t*-butoxide with *t*-amyl chloride and bromide had indicated the formation of 72% 1- for the chloride and 72.5% 1- for the bromide, whereas the present study yields the values 78% 1- for the chloride and 73% 1- for the bromide.^{6c} In our earlier study we had to rely on the refractive index for the analysis of small quantities of product isolated from the reaction mixture. Certainly more confidence can be placed on the gas chromatographic analytical procedure employed in the present study, involving direct observation of the reaction mixture.

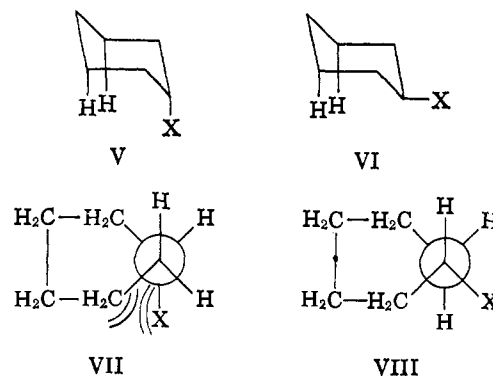
In the case of the 2-pentyl derivatives, we previously reported that elimination with potassium ethoxide yielded for the bromide, 31% 1-, 18% *cis*-2-, and 51% *trans*-2-, and for the iodide, 30% 1-, 16% *cis*-2-, and 54% *trans*-2-.^{6d} On the other hand, Saunders¹¹ finds 25% 1- for the bromide and 20% 1- for the iodide. Our analysis was based on a combination of refractive index and infrared spectrum. Again there is no doubt that the later analyses, based on gas chromatography, are the more reliable.

In any event, both Saunders' and our results clearly establish that there is a consistent trend to decreasing amounts of the 1-olefin with increasing atomic number of the halogen.¹⁷

We next turned our attention to the problem of how we might obtain an independent estimate of the steric requirements of these three halogens. In recent years considerable effort has been devoted to establishing the

(17) It is of interest to point out that Saunders is operating entirely on the Saytzeff side of the scale, whereas our results with *t*-butoxide begin with the chloride well over on the Hofmann side.

position of the axial-equatorial equilibrium for cyclohexane derivatives, C₆H₁₁X, by nmr techniques.¹⁸ Steric interactions between the axial substituent X and the 1,3-hydrogen atoms (V) are believed to be a major factor in shifting the equilibrium toward the more stable equatorial conformation (VI) where such interactions are absent.¹⁹



A comparison of the Newman projections of these cyclohexane conformers (VII, VIII) reveals that the 3,5 interactions which decrease the stability of the axial derivative are similar in nature to the interactions which are postulated in the steric interpretation to influence the stability of transition state II. Consequently, if the larger van der Waals radii of the heavier halogens increase their steric requirements, we should expect to find the *axial* cyclohexane derivative to become less and less favored, relative to the equatorial, from chlorine to bromine to iodine. On the other hand, if the covalent radius of the halogen compensates for the increase in the van der Waals radii, we might observe the axial derivative actually to be favored by the change from chloride to bromine to iodine.

Fortunately, the cyclohexyl halides have been studied by Jensen and Berlin.²⁰ They report that the amount of the axial conformer present at equilibrium is actually favored by the change from chlorine to bromine to iodine.

A word of caution may be appropriate at this point. It is not our intention to propose the axial-equatorial equilibrium of cyclohexane derivatives as a truly satisfactory model for the steric requirements of these substituents in the transition state for the E2 elimination. We merely suggest that this equilibrium, which is sensitive to the steric requirements of substituents, may be useful to estimate relative steric requirements for unsolvated groups in the absence of a more satisfactory model. In the present case, the results are of interest primarily because they reveal that the van der Waals radii alone do not provide a satisfactory measure of the effect of the halogen either in the cyclohexyl halide equilibrium or in the direction taken in the elimination reaction.

In the discussion thus far we have ignored the effect of solvation on the steric requirements. In our earlier discussion^{6c} we pointed out that in terms of the proposed interpretation ethoxide behaved as a more

(18) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 458.

(19) E. L. Eitel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, pp 42-47.

(20) A. J. Berlin and F. R. Jensen, *Chem. Ind.* (London), 998 (1960).

sterically demanding base than pyridine, whereas a consideration of the molecular dimensions alone would have predicted the opposite. However, it was proposed that ethoxide ion must be very much more solvated than pyridine and it must be the steric requirements of the solvated ion that must be considered in evaluating the effect of the base on the relative stabilities of the two possible transition states II and III.

Recently, it was reported that the E2 elimination of 2-bromobutane with potassium ethoxide yields 19% 1-butene in ethanol and 38% in *t*-butyl alcohol.^{21b} It was concluded that the steric requirements of the base could not be a factor in the direction of elimination. Leaving aside for the moment the problem of the precise species which may be involved in an elimination reaction in a solution containing potassium ethoxide in *t*-butyl alcohol, it is evident that the data are not inconsistent with the steric interpretation provided one accepts the postulate that *t*-butyl alcohol will have larger steric requirements than ethyl alcohol in solvating the alkoxide ion.

[EtOH· ⁻ OEt]	19% 1-
[<i>t</i> -BuOH· ⁻ OEt]	38% 1-
[<i>t</i> -BuOH· ⁻ O- <i>t</i> -Bu]	53% 1-

Similarly, in an elimination reaction the leaving group will be more or less solvated. Consequently, in considering the steric requirements of the leaving group such solvation should also be taken into account. It would be expected that such solvation would be most important for the fluoride and decrease to the iodide.²²

It is evident that a better understanding of the factors influencing the direction of elimination will require more systematic data than are now available, particularly with respect to the role of the solvent. We are undertaking a study of this kind.

In connection with this discussion it is of interest to point out the very important and significant study by Colter and Johnson.²³ They measured the rates and product distributions for the E2 elimination by ethoxide by a series of 2-pentyl *para*-substituted benzenesulfonates. The change in rates observed for the range of substituents examined, from *p*-nitro to *p*-amino, was comparable in magnitude to the rate change observed in the present study, from chloride to iodide. *Yet over this entire range the product distribution (per cent 1-pentene) was essentially constant: p-NO₂, 41%; p-Br, 42%; p-CH₃, 42%; p-CH₃O, 42%; p-NH₂, 42%.* Clearly, this does not appear compatible with an electronic interpretation which requires that the direction of elimination in simple alkyl derivatives be a function of the relative effectiveness of the leaving group.

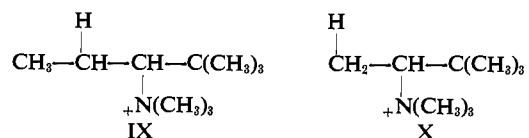
In his review Bunnett⁴ eliminated steric effects from consideration as a factor influencing the direction of

(21) (a) D. H. Froemsdorf and M. E. McCain, *J. Am. Chem. Soc.*, **87**, 3983 (1965); (b) D. H. Froemsdorf, M. E. McCain, and W. W. Wilkinson, *ibid.*, **87**, 3984 (1965).

(22) It is not known whether such solvation can be sufficiently important to account on a steric basis for the very large directional influence indicated for the elimination reactions of alkyl fluorides.¹² However, it is perhaps significant that the appreciable difference in the yield of 1-olefin observed for the elimination of secondary alkyl chlorides and bromides in hydroxylic solvents (Tables I and II) apparently vanishes in the solvent dimethyl sulfoxide. Thus, 2-bromobutane yields 31% 1-butene with potassium *t*-butoxide in dimethyl sulfoxide^{21b} and 2-chlorobutane yields 32% 1-butene under the same conditions: J. E. Hofmann, T. J. Wallace, and A. Schriesheim, *J. Am. Chem. Soc.*, **86**, 1561 (1964).

(23) A. K. Colter and R. D. Johnson, *ibid.*, **84**, 3289 (1962).

elimination in -onium salts on the basis that IX undergoes reaction with ethoxide at a rate 10-fold slower than X. He pointed out that the ethyl group in IX is con-



strained between two bulky groups. Therefore the ground-state energy of IX should be less than that of X, and he argues that a rate acceleration should be anticipated, rather than the retardation observed.

It should be apparent from our previous discussions that a rate acceleration would be anticipated *only if the strain in the initial state is relieved in the transition state*. Since the transition state for IX must involve placing the base in the highly congested environment of the secondary proton, it is not surprising that X reacts faster than IX. This would be a case of steric hindrance to elimination. *It must be kept in mind that steric strain will result in enhanced rates only when the strain in the transition state is less than the strain in the initial state.*²⁴

Finally, we wish to inject a word of caution. In our original discussion^{6e} we pointed out that the precise amount of bond making and bond breaking in the transition state will depend "upon the electronic and steric contributions of the base B, the substituents R, and the leaving group X. It is in terms of the relative importance of such structures in the transition state that the varying *cis/trans* ratios obtained in elimination reactions are to be understood."

Consequently, it is not our position that only steric factors will control the direction of elimination. It is our position that in the case of simple alkyl groups, such as 2-butyl, and simple alicyclic groups, such as neomenthyl, it is possible to account for all of the available data in terms of the effect of steric influences in decreasing the stability of the normally preferred transition state II in favor of the normally less satisfactory transition state III. As soon as unambiguous evidence becomes available that the direction of elimination in simple acyclic and alicyclic groups can be controlled by the electronic characteristics of the leaving group, we are prepared to modify the theory to incorporate this feature. However, this would not mean that the steric requirements of the leaving group will no longer need to be considered in the final theory. Indeed, all of our past experience indicates that we must consider both steric and electronic factors in arriving at satisfactory interpretations of structural effects, and there is no reason to believe that the elimination reaction will constitute an exception to this experience.

Experimental Section

Alkyl Halides. The alkyl halides were either commercial samples or were prepared from the alcohols by standard methods. The physical properties are summarized in Table III.

(24) It should be pointed out that Bunnett's argument rests on an assumption of steric acceleration in the bimolecular elimination reaction of IX. Although steric acceleration has been demonstrated in many cases of unimolecular reactions, we know of no authentic case where steric acceleration has been demonstrated in a bimolecular reaction. Steric hindrance is the recognized pattern of behavior for such reactions. Consequently, we believe that this argument provides a highly dangerous basis for his rejection of steric effects as a significant factor in bimolecular elimination reactions.

Table III. Physical Constants of Alkyl Halides

Compound	Bp, °C (mm)	Lit bp, °C (mm)	n_D^{20}	Lit n_D^{20}
<i>t</i> -Amyl chloride	84	85	1.4040	1.4046
<i>t</i> -Amyl bromide			1.4418	1.4412
<i>t</i> -Amyl iodide	28 (12)	35 (19)	1.4950	1.4949
2-Butyl chloride	67	68	1.3963	1.3953
2-Butyl bromide	91	91	1.4344	1.4348
2-Butyl iodide	52 (65)	120	1.4989	1.4990

Gas chromatographic examination on a Carbowax column showed only single peaks with the definite absence of observable peaks corresponding to the alcohols or olefins.

***t*-Butoxide Solution.** The *t*-butyl alcohol was dried by refluxing over calcium hydride and then distilled at atmospheric pressure. Potassium metal in the appropriate amount was added to the purified alcohol under nitrogen atmosphere and the solution was refluxed until the potassium had dissolved. The concentration was then adjusted to 1.0 *M*.

Product Analysis. Solutions of the olefins were prepared in the 1.0 *M t*-butoxide solution and allowed to stand under the conditions of the elimination reaction for periods of time which were much longer than the reaction time. No loss or isomerization of the butenes or methylbutenes was observed. It was also demonstrated that the reaction mixture could be injected directly into the chromatograph and the analysis achieved with a reproducible precision of better than $\pm 0.5\%$.

Product Determinations. The alkyl halide was weighed in a volumetric flask to provide the desired concentration and the flask was filled to the mark with 1 *M* potassium *t*-butoxide in *t*-butyl alcohol. Aliquots were sealed in ampoules and these were maintained at 50° for the appropriate time. The ampoules were cooled, opened, and immediately subjected to gas chromatographic analysis on an Aerograph instrument containing a 15-ft adiponitrile column (25° for the methylbutenes, 0° for the butenes). Typical experimental results are summarized in Table IV.

The yield of olefin was established by comparing the solutions with an external standard. Within the limits of the experimental uncertainty, $\pm 2\%$, the analyses revealed 100% yields. Moreover, no peaks were found other than the olefins and *t*-butyl alcohol. Consequently, the elimination reaction must proceed quantitatively, without any significant ether formation.

Rate Measurements. The rates of the E2 reactions were followed by measuring the amount of olefin formed as described above. The concentration of base was 1.0 *M* and the halide 0.1 *M*, so that the eliminations could be treated as a pseudo-first-order reaction.

For the E1 reaction, the rate of olefin production was followed

Table IV. Product Compositions in the Reactions of Alkyl Halides with Potassium *t*-Butoxide in *t*-Butyl Alcohol at 50°

Alkyl halide	Time, days	Product composition, %		
		1- ^a	<i>trans</i> -2 ^b	<i>cis</i> -2
<i>t</i> -Amyl chloride	3	77.6	22.4	
	4	77.3	22.7	
	7	77.8	22.2	
<i>t</i> -Amyl bromide	3	69.0	31.0	
	4	69.3	30.7	
	5	69.4	30.6	
<i>t</i> -Amyl iodide	0.5 hr	51.2	48.8	
	5.0 hr	51.2	48.8	
2-Butyl chloride	1	68.3	17.7	13.8
	2	66.4	19.8	13.9
	4	66.8	18.6	14.5
	1	53.4	27.7	18.9
2-Butyl bromide	2	53.6	27.6	18.8
	4	53.6	27.6	18.8
	1	33.8	44.3	21.9
2-Butyl iodide	4	33.3	44.7	22.0

^a 1-Butene or 2-methyl-1-butene. ^b *trans*-2-Butene or 2-methyl-2-butene.

in *t*-butyl alcohol, using potassium carbonate to neutralize the acid produced.

Product Distribution in the E1 Reaction. The rates of the E1 reaction were very slow. Consequently, the reaction mixtures in ampoules were allowed to run for several months and the olefins were analyzed periodically, yielding the following results: *t*-amyl chlorides, 25% 1-; bromide, 28% 1-; iodide, 21% 1-.

Correction for the E1 Contribution. The comparison of first- and second-order processes is rather complicated mathematically. Therefore a graphical method was employed to dissect the first-order contribution from the over-all base-induced reactions. These graphs were prepared by plotting the per cent reaction vs. time for both the solvolysis and the over-all reaction. The percentage first-order contribution then was subtracted from the over-all product distribution using the E1 distributions which were measured previously.

In the case of *t*-amyl chloride the estimated E1 reaction was only 1% of the E2 reaction, so no correction was made. For *t*-amyl bromide the graph shows that the E1 reaction contributes 6% of the total reaction. This changes the per cent of 1-olefin for pure E2 to 73% (Table II). Finally, in the case of the iodide the graph indicates that 25% of the total reaction is due to a first-order process. This changes the per cent of 1- from the observed 51% (Table IV) to 60% (Table II).