

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Steric Effects in Elimination Reactions. X. Steric Strains as a Factor in Controlling the Direction of Bimolecular Eliminations. The Hofmann Rule as a Manifestation of Steric Strain

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It was previously proposed that the direction of bimolecular eliminations is controlled by the negative stabilization of the incipient olefin and by steric strains in the transition state. Such strains in the transition state can be increased by (1) increasing the steric requirements of alkyl groups attached to the incipient double bond, (2) increasing the steric requirements of the attacking base and (3) increasing the steric requirements of the leaving group. Since such strains are more important in the transition state leading to the more alkylated of two possible olefins (Saytzeff rule) than in the transition state leading to the less branched of the two possible olefins (Hofmann rule), an increase in the steric effects by any one of these three methods, or by any combination of them, should result in a shift in the direction of elimination from Saytzeff toward Hofmann. The generality of this concept is tested in a number of systems. The results fully support the conclusion that the Hofmann rule is a manifestation of steric effects in the transition state. There appears to be no need to attribute any significant portion of the Hofmann-type elimination of the 'onium salts to a polar factor resulting from the formal charge carried by the 'onium group.

It was proposed previously that steric effects play an important role in controlling the direction of bimolecular elimination reactions.^{2a} It was pointed out that it should be possible to increase steric strain in the transition state for the elimination reaction by (1) increasing the steric requirements of the alkyl groups on the incipient double bond, (2) increasing the steric requirements of the attacking base and (3) increasing the steric requirements of the leaving group.^{3,4}

According to the proposal such strains should be more important in the transition state leading to the more alkylated of two possible olefins than in the transition state leading to the less alkylated olefin. Consequently an increase in steric strain in the transition state by any of the three methods mentioned above, or by any combination of them, should lead to a decreased yield of the more alkylated of the possible olefins (Saytzeff rule) and thus to an increased yield of the less alkylated (Hofmann rule).

In the first paper of this group it was demonstrated that an increase in the steric requirements of R (R = Me, Et, *i*-Pr and *t*-Bu) in the tertiary bromides, RCH₂CBr(CH₃)₂, does indeed result in an increased tendency toward elimination in accordance with the Hofmann rule^{2a} (Fig. 1).

In the second paper it was shown that an increase in the steric requirements of the alkoxide base, RO⁻ (R = Et, *t*-Bu, *t*-Am, Et₃C), used in the elimination reaction likewise results in an increased tendency of both secondary and tertiary alkyl bromides to undergo elimination in accordance with the Hofmann rule^{2b} (Fig. 2). Rate data demonstrated that the

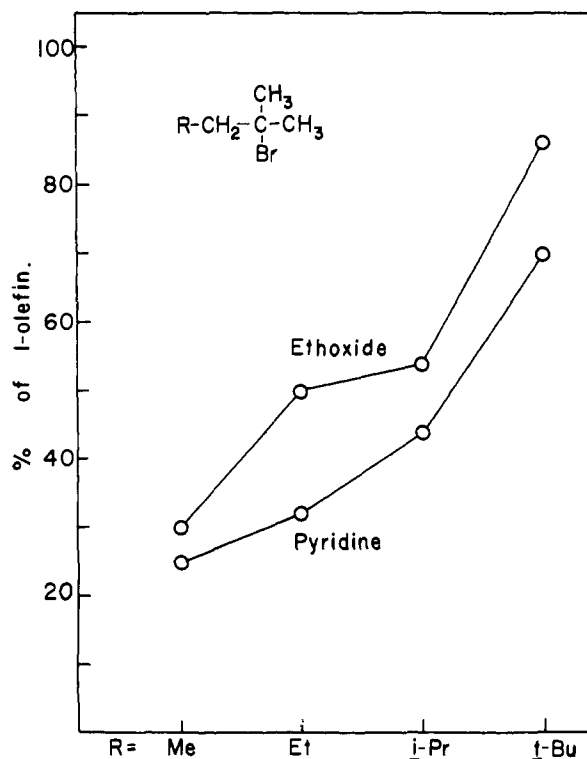


Fig. 1.—Effect of increasing steric requirements of R in the tertiary bromides, RCH₂CBr(CH₃)₂, on the direction of bimolecular elimination.

change in orientation could be attributed primarily to a decreased rate of attack of the hindered bases on the more sterically hindered secondary and tertiary hydrogen atoms.^{2b} The generality of the phenomenon is indicated by the third paper. It was observed that a shift in orientation from Saytzeff to Hofmann could be realized by the use of a series of pyridine bases (pyridine, 2-picoline, 2,6-lutidine) of increasing steric requirements^{2c} (Fig. 3).

In the fourth paper of the present group we utilized the 2-pentyl system to test the proposal that the yield of 1-olefin should increase with increasing steric requirements of the leaving group^{2d,5} (Fig. 4).

(5) C. H. Schramm, *Science*, **112**, 367 (1950).

(1) Post-doctorate Assistant at Purdue University, 1951–1953, on a contract supported by the Office of Naval Research for the study of "Steric Strains in Chemical Reactions."

(2) (a) H. C. Brown, I. Moritani and M. Nakagawa, *THIS JOURNAL*, **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).

(3) This interpretation of the role of steric effects in elimination reactions was originally presented to the Organic Division of the American Chemical Society at the Meeting in Atlantic City, Sept., 1952. A communication reporting certain of the results has been published: H. C. Brown and I. Moritani, *THIS JOURNAL*, **75**, 4112 (1953).

(4) For an alternative viewpoint of the factors controlling the direction of bimolecular elimination see M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour and G. A. Maw, *J. Chem. Soc.*, 2093 (1948).

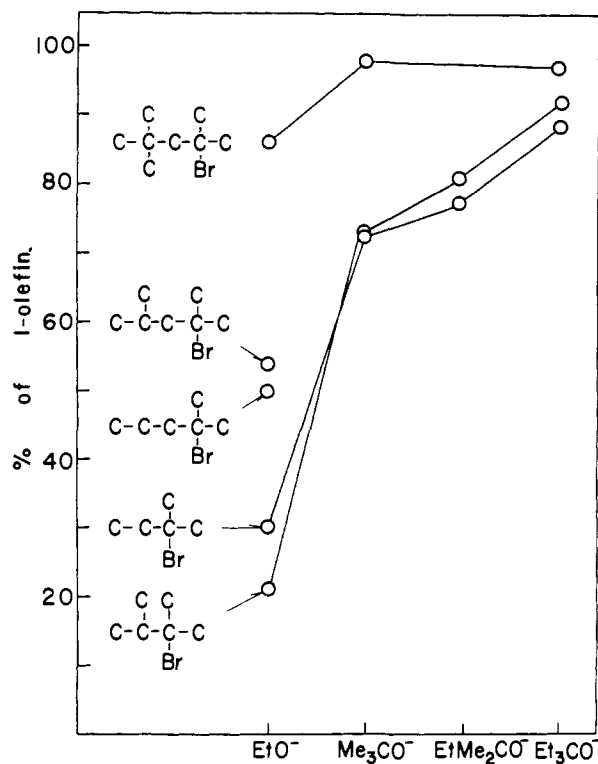


Fig. 2.—Effect of increasing steric requirements of the alkoxide base on the direction of bimolecular elimination.

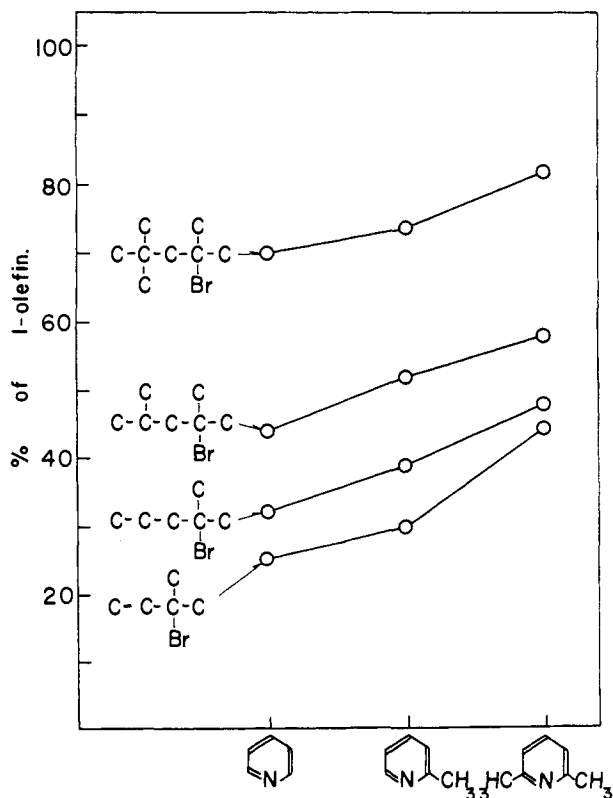


Fig. 3.—Effect of increasing steric requirements of the pyridine base on the direction of bimolecular elimination.

Finally, in the present paper we examine the generality of the results. Thus it was previously

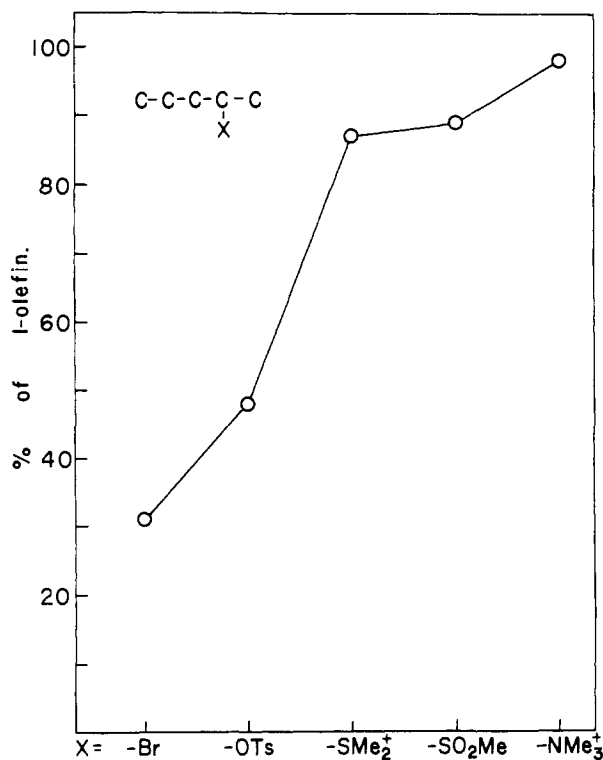


Fig. 4.—Effect of the steric requirements of the leaving group on the direction of bimolecular elimination.

shown that in the reaction of 2,4,4-trimethyl-2-bromopentane with pyridine bases, the yield of 1-olefin increases with the increasing steric requirements of the pyridine base. In the present paper we have treated the corresponding trimethylammonium derivative with the three pyridine bases in order to ascertain whether in this reaction there occurs a similar increase in the yield of 1-olefin with increasing steric requirements of the base.

In the previous paper we advanced arguments to support the thesis that because of the compensating effect of increasing van der Waals radii and covalent radii, there should be little difference in the steric requirements of chlorine, bromine and iodine. In support of this conclusion, very little difference was observed in the elimination reactions of 2-bromo- and 2-iodopentane.^{2d} In the present paper we have examined the elimination reactions of several related chlorides and bromides.

Finally, arguments have been presented to favor the view that the steric requirements should increase in the order $-\text{Hal} < -\text{OSO}_2\text{Tol} < -\text{SMe}_2^+ < -\text{NMe}_3^+$.^{2d} Elimination reactions on several tosylates and quaternary ammonium compounds were carried out to provide a test of the generality of this conclusion.

All of the data now available permit a detailed examination of the individual and combined effects of the three factors previously proposed as controlling steric strains in the transition state.

Results

2,4,4-Trimethyl-2-aminopentane was converted into 2,4,4-trimethyl-2-dimethylaminopentane by treatment with formaldehyde and formic acid. Re-

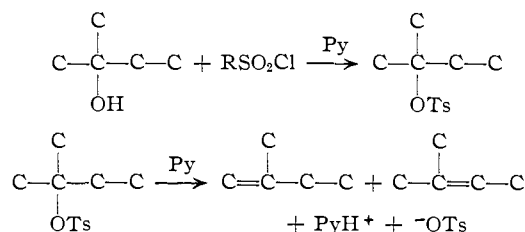
action with methyl iodide yielded the trimethylammonium derivative. The salt reacted smoothly with the pyridine bases to liberate olefin and trimethylamine. The diisobutylene obtained on treatment with pyridine contained 88% of 2,2,4-trimethyl-1-pentene. This rose to 95% with 2-picoline, and to 99% with 2,6-lutidine. In treating the corresponding bromide with these same three bases there were realized products containing 70, 74 and 82% of the 1-olefin.^{2c}

t-Amyltrimethylammonium iodide was synthesized by a similar series of reactions. On elimination with 2,6-lutidine there was obtained a product containing 92.5% yield of the 1-olefin, corresponding to the 99% composition realized in the case of the more bulky derivative, 2,4,4-trimethyl-2-pentyltrimethylammonium iodide. On treatment with potassium ethoxide, *t*-amyltrimethylammonium iodide yielded a product containing 93% of 2-methyl-1-butene, as contrasted with 86% of the 1-olefin observed in the corresponding reaction of *t*-amyltrimethylsulfonium iodide.⁶

Treatment of *t*-amyl chloride with potassium *t*-butoxide yielded 72% of 2-methyl-1-butene. This is essentially identical with that previously observed for the bromide.^{2b} Similarly, treatment of 2,4,4-trimethyl-2-pentyl chloride with 2,6-lutidine yielded products containing 83% of the 1-olefin, essentially identical with the 81-82% yield previously realized for the bromide.^{2c}

In examining the relative effects of bromine and tosylate it was observed that the 53% yield of 1-butene obtained in the reaction of potassium *t*-butoxide with 2-bromobutane^{2b} was increased to 62% in the reaction of the same base with 2-butyl tosylate. Similarly, the yield of 66% of 1-pentene obtained in the same reaction utilizing 2-bromopentane^{2b} was increased to 73% in the case of the tosylate.

It appeared desirable to extend this comparison of bromides and tosylates to tertiary alkyl derivatives. However, at the time this study was made *t*-alkyl derivatives of sulfonic acids had not been synthesized. We therefore attempted to achieve our objective by treating the tertiary alcohol with *p*-toluenesulfonyl chloride and a large excess of pyridine under reflux. It was argued that the conditions could be conducive first for the formation of the tosyl ester⁷ and then for the elimination reaction under the influence of the pyridine.



Under these conditions *t*-amyl alcohol was converted into olefin in a yield of 69%. The 1-olefin content of the product was 37% as contrasted to 30% obtained in the corresponding reaction of *t*-

(6) E. D. Hughes, C. K. Ingold and L. I. Woolf, *J. Chem. Soc.*, 2084 (1948).

(7) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

amyl bromide. Similarly, 2,4,4-trimethyl-2-pentanol was converted into diisobutylene in a yield of 75%. The product consisted of 75% 1-olefin as compared to 70% realized in the pyridine dehydrohalogenation of the corresponding bromide. Finally, 2,3-dimethyl-2-butanol was converted under these conditions into the corresponding olefins in a yield of 73%. The composition of the product was 43% 2,3-dimethyl-1-butene as compared to the 10% realized in the reaction of pyridine with the bromide.

Treatment of *t*-amyl alcohol with *p*-toluenesulfonyl chloride in refluxing toluene in the absence of pyridine did not result in olefin formation. We do not claim to have established the mechanism of this elimination reaction. However, in the absence of any evidence to the contrary we shall assume that the elimination proceeds through the formation of the *t*-alkyl tosylate and its reaction with pyridine.

The experimental results are summarized in Table I.

TABLE I
COMPOSITION OF OLEFINS FORMED IN THE ELIMINATION REACTIONS OF SELECTED DERIVATIVES

Compound	Base	Olefin composition, %	
		1-	2-
<i>t</i> -Amyltrimethylammonium iodide	1 <i>M</i> EtOK	93	7
	2,6-Lutidine	92.5	7.5
2,4,4-Trimethyl-2-pentyltrimethylammonium iodide	3 <i>M</i> NaOH	100	0
	Pyridine	88	12
	2-Picoline	95	5
	2,6-Lutidine	99	1
<i>t</i> -Amyl chloride	1 <i>M</i> <i>t</i> -BuOK	72	28
<i>t</i> -Amyl bromide ^b	1 <i>M</i> <i>t</i> -BuOK	72.5	27.5
2,4,4-Trimethyl-2-chloropentane			
	2,6-Lutidine	83	17
2,4,4-Trimethyl-2-bromopentane ^c			
	2,6-Lutidine	81	19
2-Butyl tosylate	1 <i>M</i> <i>t</i> -BuOK	62	38
2-Pentyl tosylate	1 <i>M</i> <i>t</i> -BuOK	73	27
(<i>t</i> -Amyl tosylate) ^a	Pyridine	37	63
(2,3-Dimethyl-2-butyl tosylate) ^a	Pyridine	43	57
(2,2,4-Trimethyl-4-butyl tosylate) ^a	Pyridine	75	25

^a Formation as an intermediate in the reaction is assumed.
^b Ref. 2b. ^c Ref. 2c.

Discussion

It was originally observed by Hofmann that elimination from a quaternary ammonium salt occurred in such a direction as to produce the least alkylated olefin.⁸ Saytzeff, however, pointed out that secondary or tertiary halides underwent elimination to form the most highly alkylated olefin.⁹

It is well known that the stability of the double bond increases with the number of alkyl substituents.¹⁰ Thus the heats of hydrogenation decrease with the number of methyl groups in the olefins in (kcal./mole): ethylene, -32.8; propylene, -30.1;

(8) A. W. Hofmann, *Ann.*, **78**, 253 (1851); **79**, 11 (1851).

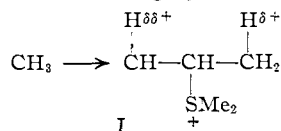
(9) A. Saytzeff, *ibid.*, **179**, 296 (1875).

(10) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *THIS JOURNAL*, **58**, 137 (1936).

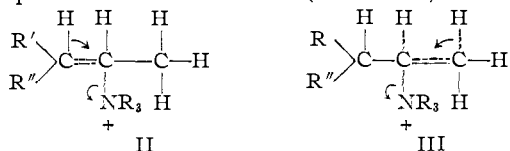
isobutylene, -28.4 ; trimethylethylene, -26.9 ; tetramethylethylene, -26.6 .¹⁰ This increase in stability is presumably the result of increasing possibilities for stabilization of the double bond through hyperconjugative interactions with the alkyl groups.¹¹ It was suggested that similar hyperconjugative interactions could occur with the incipient double bond in the transition state for bimolecular elimination and that such interactions provided a reasonable explanation for eliminations which proceed to give the most highly alkylated olefin (Saytzeff rule).⁴

The establishment of a satisfactory theoretical basis for eliminations which proceed to give the least alkylated olefin (Hofmann rule) has been more difficult. In this case it is necessary to account for the reaction proceeding in a direction so as to give the thermodynamically less stable product.

It was shown by Hughes, Ingold and their co-workers that alkyldimethylsulfonium salts also underwent elimination in accordance with the Hofmann rule.⁴ Consequently they concluded that the formal positive charge in the 'onium group was responsible for that type of control represented by the Hofmann rule. They suggested that under the influence of the positive charge there is a flow of electrons from the β -carbon atoms. This is resisted by the inductive effects of alkyl and, especially, branched alkyl substituents, resulting in a preferential attack of the base at the least heavily alkylated β -carbon atom (I). Such an attack would lead to the formation of the less highly branched olefin.



An alternative interpretation was advanced by Schramm.⁵ He suggested that steric effects control the direction of elimination in 'onium salts. He pointed out that in elimination from a quaternary salt ($R' = \text{alkyl}$, $R'' = \text{alkyl or H}$), there were two possible transition states (II and III).



He suggested that the partial formation of the double bond in the transition state would require the groups R' , R'' and $^+NR_3$ to lie in a single plane in the transition state. This would introduce serious steric difficulties, so that the alternative transition state III would be favored. Although we are in essential agreement with Schramm's thesis that steric effects are the basis of the Hofmann rule, we believe that there are serious difficulties with the transition state he proposes.

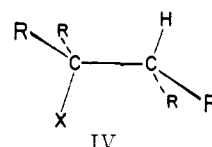
We have previously observed that the solvolysis of 2,4,4-trimethyl-2-chloropentane produces predominantly 2,4,4-trimethyl-1-pentene.¹² This case of Hofmann-type elimination in an E-1 reaction led

(11) R. S. Mulliken, C. A. Rieke and W. G. Brown, *THIS JOURNAL*, **63**, 41 (1941).

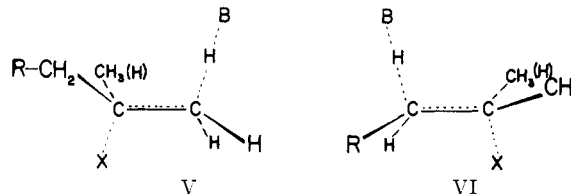
(12) H. C. Brown and H. L. Berneis, *ibid.*, **75**, 10 (1953).

us to question the interpretation based on the existence of a positive charge in the group undergoing elimination.⁴ Since steric effects had provided a satisfactory explanation for the preferred formation of 2,4,4-trimethyl-1-pentene in the unimolecular elimination reaction, we were led to a consideration of the possible role of steric effects in controlling the direction of elimination in bimolecular reactions.

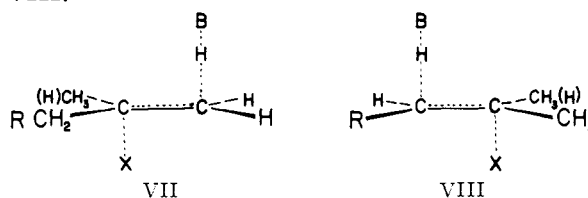
Convincing evidence is now available in support of the conclusion that in bimolecular elimination reactions the preferred transition state will contain the four atoms concerned in the reaction in a planar *trans* arrangement.^{13,14,15} It is therefore to be expected that in a substituted ethane derivative which is undergoing bimolecular elimination the molecule will assume a conformation which places the hydrogen atom and the leaving group in a *trans* arrangement in the same plane as the two central atoms (IV).



The transition states for the elimination reaction may therefore be represented as in V and VI.



It should be recognized that this represents a possible extreme transition state for the elimination reaction. With increasing formation of the double bond the transition state will approach more closely the geometrical representation shown in VII and VIII.¹⁶



In general, elimination reactions are strongly exothermic processes. The transition state may be ex-

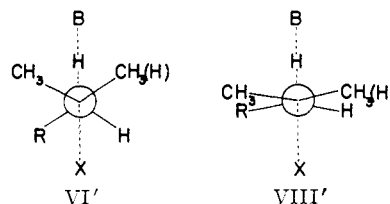
(13) W. Hückel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940).

(14) S. J. Cristol, *THIS JOURNAL*, **69**, 338 (1947); **71**, 1894 (1949);

S. J. Cristol, N. L. Hause and J. S. Meek, *ibid.*, **73**, 674 (1951).

(15) D. H. R. Barton and E. Miller, *ibid.*, **72**, 1066 (1950).

(16) The geometries of these transition states may be better understood by utilizing the end-on projections recommended by Professor M. S. Newman.



pected therefore to resemble the reactants (V, VI) more closely than the products (VII, VIII).¹⁷ On the basis of this and other considerations we shall utilize the transition states V and VI in considering the possible role of steric effects on the direction of bimolecular elimination reactions.

It should be recognized that the transition states represented by V and VI represent an extreme in the probable structure and the actual state will approach the other extreme (VII and VIII) to some degree, depending 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. Since this phase of the problem is currently under investigation in other laboratories, we shall not attempt to discuss those factors which control *cis-trans* isomer yields.^{18,19}

It is considered that in the absence of appreciable steric effects the transition state represented in VI will be more stable than V because of the greater possibilities of hyperconjugation between the incipient double bond and the alkyl groups.⁴ The reaction will therefore proceed preferentially through this transition state to give a predominant yield of the 2-olefin (more highly alkylated olefin—Saytzeff rule).

This situation will be altered by the existence of steric effects. Such steric effects should arise from any one of three changes: (1) an increase in the steric requirements of the alkyl group R, (2) an increase in the steric requirements of the attacking base B and (3) an increase in the steric requirements of the leaving group X.

It should be apparent from the diagram VI that an increase in the steric requirements of the group R should result in increased steric interactions between the groups R and X. Such interactions will make the attainment of the transition state VI more costly in energy. On the other hand, an increase in the steric requirements of R should have much less effect on the transition state represented by V.

On the basis of these considerations an increase in the steric requirements of R would be expected to result in a decreased tendency for the reaction to proceed through the transition state VI (Saytzeff rule elimination) and an increased tendency for the reaction to proceed through the less strained transition state V (Hofmann rule elimination). Such a change in the direction of elimination with changing steric requirements of R has been observed.^{2a}

Similarly an increase in the steric requirements of the base B would be expected to result in much larger steric interactions in the transition state leading to the 2-olefin VI than in that leading to the 1-olefin V. Consequently, an increase in the steric requirements of the base would be expected to favor the reaction leading through the less strained transition state V. Again the experimental results reveal

a marked tendency for the reaction to change from Saytzeff-type elimination to Hofmann-type elimination with increasing steric requirements of the base.^{2b,c}

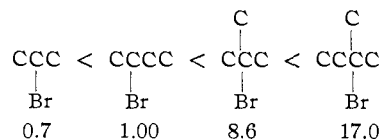
Finally, an increase in the steric requirements of X should increase the steric interactions between R and X. (The situation should be quite identical to the effects of an increase in the steric requirements of R, as discussed previously.) Consequently, on the basis of this model we reach the same conclusion as that reached by Schramm on the basis of his proposed transition state. Both in the preceding paper^{2d} and in the present paper we have reported considerable experimental data to support the conclusion that there is observed a regular shift from Saytzeff-type to Hofmann-type elimination with increasing steric requirements of the group undergoing elimination.

The transition states shown in V and VI have been simplified to show eliminations which can proceed to give 1- and 2-olefins of the type which have been studied in the present group of papers. It should be apparent that both the transition states and the discussion can be generalized to include all eliminations which proceed to give the most alkylated or the least alkylated of the possible olefins.

Thus far in the discussion we have considered only the effect of one of these three factors at one time. However, each of these factors should operate independently and the simultaneous operation of any two or of all three should be reflected in a cumulative change. For example, the reaction of *t*-amyl bromide with pyridine produces 25% of the 1-olefin. An increase in the steric requirements of the base to 2,6-lutidine increases the yield of 1-olefin to 44.5%. An increase in the steric requirements of the alkyl group, as in 2,4,4-trimethyl-2-bromopentane, causes the 1-olefin content of the product to rise to 81.5%, while an increase in the steric requirements of the leaving group to $-NMe_3^+$ results in a further increase in the 1-olefin present in the product to 99%.

For convenience in following the individual and cumulative effects of increasing steric strain in the transition state resulting from increasing steric requirements of each of the three different factors discussed above, the available data are summarized in Table II.

Hughes and Ingold and their co-workers⁴ based their interpretation of the factors at the basis of the Hofmann rule in part on rate data. They pointed out that the observed order of bimolecular elimination rates of secondary and tertiary alkyl bromides was in agreement with that predicted on the basis of hyperconjugative stabilization of the transition state (sodium ethoxide in ethanol at 25°)



On the other hand, in the corresponding reactions of the alkyldimethylsulfonium salts, a different order was observed (sodium ethoxide in ethanol at 25°).

(17) G. S. Hammond, *THIS JOURNAL*, **77**, 334 (1955).

(18) D. Y. Curtin, *Record Chem. Prog.*, **12**, 111 (1954).

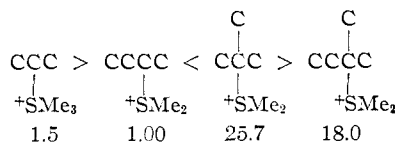
(19) D. J. Cram, F. D. Green and C. H. Depuy, *THIS JOURNAL*, **78**, 790 (1956).

TABLE II

PERCENTAGE OF 1-OLEFIN FORMED IN THE BIMOLECULAR ELIMINATION REACTIONS OF VARIOUS 2-SUBSTITUTED DERIVATIVES

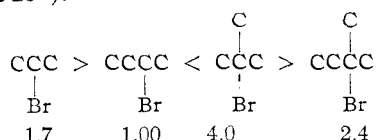
Compound	X	Base						
		Pyridine	2-Picoline	2,6-Lutidine	EtO ⁻	<i>t</i> -BuO ⁻	<i>t</i> -AmO ⁻	Et ₃ CO ⁻
2-Butyl	Br				19 ^g	53 ^b		
	OTs					62 ^e		
	SMe ₂ ⁺				73 ⁱ			
2-Pentyl	Br				31 ^{d,h}	66 ^b		
	I				30 ^d			
	OTs				48 ^d	73 ^e		
	SMe ₂ ⁺				87 ^d			
	SO ₂ Me				89 ^d			
	NMe ₃ ⁺				98 ^d			
2,3-Dimethyl-2-butyl	Br	10 ^c	18 ^c	37.5 ^c	21 ^b	73 ^b	81 ^b	92 ^b
	OTs ^f	43 ^e						
<i>t</i> -Amyl	Cl					72		
	Br	25 ^a	30 ^c	44.5 ^c	30 ^{a,k}	72.5 ^b	77.5 ^b	88.5 ^b
	OTs ^f	37 ^e						
	SMe ₂ ⁺				86 ^j			
2-Methyl-2-pentyl	Br	32 ^a	39 ^c	48 ^c	50 ^g			
	Cl	44 ^a	52 ^c	58 ^c	54 ^a			
2,4-Dimethyl-2-pentyl	Br							
	Cl							
	Br	70 ^a	74 ^c	82 ^c	86 ^a	98 ^b		97 ^b
	OTs ^f	75 ^e						
2,4,4-Trimethyl-2-pentyl	Br							
	NMe ₃ ⁺	88 ^e	95 ^e	99 ^e	100 ^e			

^{a,b,c,d} Refer to footnote 2. For precise experimental conditions refer to the individual papers. ^e Present paper. ^f Formation of tosylate assumed. See results section of present paper. ^g H. J. Lucas, R. T. Dillon and W. G. Young, *THIS JOURNAL*, 52, 1949 (1930), report 17.5% 1-; M. L. Dhar, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2058 (1948), report 20% 1-. ^h H. J. Lucas, T. P. Simpson and J. M. Carter, *THIS JOURNAL*, 47, 1462 (1925), report 29% 1-. ⁱ E. D. Hughes, C. K. Ingold, G. A. Maw and L. I. Woolf, *J. Chem. Soc.*, 2077 (1948). ^j E. D. Hughes, C. K. Ingold and L. I. Woolf *ibid.*, 2084 (1948). ^k M. L. Dhar, E. D. Hughes and C. K. Ingold, *ibid.*, 2065 (1948), report 29% 1-.



They attributed this altered order to electronic flows in the hydrocarbon group rendered important by the positive charge on the sulfonium group.

However, we observed an identical order in the reaction of potassium *t*-butoxide with the corresponding bromide (potassium *t*-butoxide in *t*-butyl alcohol at 25°).

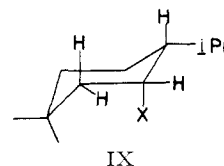


It does not appear necessary, therefore, to attribute the order observed in the alkyldimethylsulfonium ions to the polar effect of the charge. Instead the altered orders in both the reaction of sodium ethoxide with the alkyldimethylsulfonium ions and in the reaction of potassium *t*-butoxide with the alkyl bromides is simply accounted for in terms of the steric interactions encountered in the transition states V and VI. In other words, the decreased reactivities of the 2-butyl and *t*-amyl derivatives, which is the basis of the altered order, is attributed to increased steric strain arising from the large steric requirements of the dimethylsulfonium group in the one case and from the large steric requirements of the base in the other.

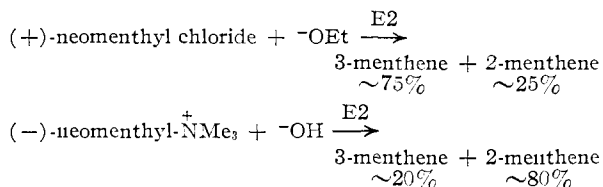
The predominant formation of the 1-olefin in the

elimination reaction of 2-pentylmethyl sulfone,^{2d} a molecule which does not carry a formal charge, provides further support for the steric interpretation. Finally, the success of the steric interpretation in providing a simple, consistent explanation for such a large mass of data as that summarized in Table II argues further for its probable correctness.

One further argument may be mentioned. 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 (IX). The elimination reactions of neo-



menthyl derivatives have been studied by Hückel and his co-workers²⁰ and it was pointed out by Ingold and his co-workers that markedly different orientations are achieved in the treatment of neomenthyl chloride and neomenthyltrimethylammonium ion with base.⁴



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

TABLE III
SUMMARY OF EXPERIMENTAL DATA ON THE YIELD AND COMPOSITION OF OLEFINS FORMED IN VARIOUS ELIMINATION REACTIONS

Compound, RX	g.		Base, ml.	Olefin yield,		Olefin composition		
	g.	mole		g.	%	n_D^{20}	1-%	2-%
<i>t</i> -Amyltrimethylammonium iodide	11.4	0.044	50, 4 M KOEt	3.61	84	1.3786	93	7
	8.74	.033	50, 2,6-lutidine	2.28	79	1.3785	92.5	7.5
2,4,4-Trimethyl-2-pentyltrimethylammonium hydroxide ^a	6.10	.030	100, 3 M NaOH	2.59	70	1.4086	100	0
2,4,4-Trimethyl-2-pentyltrimethylammonium iodide	30.0	.100	100, pyridine	8.02	80	1.4095	88	12
	10.5	.035	35, 2-picoline	3.38	86	1.4090	95	5
	7.8	.026	50, 2,6-lutidine	2.51	96	1.4087	99	1
<i>t</i> -Amyl chloride	10.66	.100	100, 1 M <i>t</i> -BuOK	6.27	91	1.3805	72	28
2,4,4-Trimethyl-2-pentyl chloride	5.00	.033	40, 2,6-lutidine	2.63	87	1.4098	83	17
2-Butyl tosylate	17.60	.074	150, 1 M <i>t</i> -BuOK				53	46
2-Pentyl tosylate	22.14	.091	150, 1 M <i>t</i> -BuOK	5.39	91	1.3738	66	34
(<i>t</i> -Amyl tosylate) ^b	8.80 ^c	.100	100, pyridine	4.85	69	1.3839	36	64
	10.0 ^c	.113	100, pyridine	6.56	91	1.3839	36	64
(2,3-Dimethyl-2-butyl tosylate) ^b	10.2 ^c	.100	100, pyridine	6.18	74	1.4031	42	58
	10.2 ^c	.100	100, pyridine	6.13	73	1.4030	43	57
(2,4,4-Trimethyl-2-pentyl tosylate) ^b	13.0 ^c	.100	100, pyridine	8.25	75	1.4104	75	25

^a Measured as a standard solution in water. ^b Formation as an intermediate in the reaction assumed. ^c Alcohol weight.

It was considered that this change in orientation favored the polar interpretation of the Hofmann rule.

As already stated, the steric interpretation cannot account for these results. With a given base, the steric effects of the group X should be essentially constant for attack at the secondary as compared to attack at the tertiary hydrogen. The relative conversion to 2- or 3-menthene should then be controlled essentially by the relative hyperconjugative stabilization of the two transition states.²¹

A careful examination of Hückel's experimental data resolved the difficulty. According to the experimental data all neomenthyl derivatives yield 3-menthene preferentially (80 ± 10%). There appears to have been an error in entering the results of the neomenthyltrimethylammonium ion (80% 3-menthene, 20% 2-menthene) in the table in the discussion portion of the paper. More recently Read has confirmed this conclusion. In a new experimental study of the elimination of neomenthyltrimethylammonium hydroxide, he finds 90% 3-menthene and 10% 2-menthene.²²

In conclusion, then, all of the available data support the interpretation that elimination in accordance with the Saytzeff rule represents control by the hyperconjugative factor,⁴ whereas elimination in accordance with the Hofmann rule represents control by the steric factor.

Experimental Part

Materials.—*t*-Amyl alcohol was converted into *t*-amylamine (b.p. 76° at 745 mm., n_D^{20} 1.3993) by the procedure of Ritter and Kalish.²³ This was transformed into *t*-amyl-dimethylamine (b.p. 117–118° at 744 mm.) by treatment with paraformaldehyde and formic acid. Finally, reaction with methyl iodide in ethyl ether led to the formation of white crystals of *t*-amyltrimethylammonium iodide. After recrystallization from absolute ethanol, the salt decomposed at 225°. *Anal.* Calcd. for C₈H₂₀NI: I, 49.35. Found: I, 49.48. 2,4,4-Trimethyl-2-aminopentane (Rohm and Haas) was converted into the dimethyl derivative in the same manner (b.p. 173–175° at 740 mm.) and then treated

(21) The ratio should, of course, be altered by a change in the steric requirements of the attacking base.

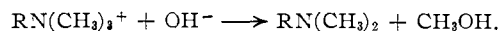
(22) N. L. McNiven and J. Read, *J. Chem. Soc.*, 153 (1952).

(23) J. J. Ritter and J. Kalish, *This Journal*, **70**, 4048 (1948).

with excess methyl iodide to form 2,4,4-trimethyl-2-pentyltrimethylammonium iodide. After recrystallization from ethanol, the product decomposed at 255–258°. *Anal.* Calcd. for C₁₁H₂₅NI: N, 4.69; I, 42.42. Found: N, 4.53; I, 42.57.

The remaining materials were either prepared or purified as described in other papers in this series.

Elimination Reactions of the *t*-Alkyltrimethylammonium Salts.—2,4,4-Trimethyl-2-pentylammonium iodide was dissolved in water and treated with excess silver oxide to form the corresponding quaternary ammonium hydride. A total of 12.0 g. (0.3 mole) of sodium hydroxide was added to 100 cc. of 0.3003 *N* solution of the quaternary hydroxide. The solution was heated to 100° and the olefin and trimethylamine formed were distilled out and collected together with a small amount of water. Water was added to the flask periodically to maintain the concentrations essentially constant. The decomposition was relatively slow requiring 24 hours to be completed. There was obtained 2.59 g. of the olefin, a yield of 70%. The refractive index, n_D^{20} 1.4086, indicated a composition of 100% 2,4,4-trimethyl-1-pentene. The low yield is presumably due to the side reaction



t-Amyltrimethylammonium iodide was treated with potassium ethoxide by the identical procedure previously described for 2-pentyltrimethylammonium iodide.²⁴

The following procedure is typical of that used to study the elimination reactions of the *t*-alkyltrimethylammonium iodides under the influence of the pyridine bases.

2,4,4-Trimethyl-2-pentyltrimethylammonium iodide, 7.80 g., was dissolved in 50 cc. of 2,6-lutidine. The reaction mixture was heated under reflux for 12 hours, the olefin being collected as it formed in a Todd micro fractionating column. There was obtained 2.51 g. of diisobutylene with n_D^{20} 1.4087, indicating a composition of 99% 2,4,4-trimethyl-1-pentene.

Elimination Reactions of the Tosylates.—The secondary alkyl tosylates, 2-butyl and 2-pentyl, were synthesized and weighed quantities were added to 1 *M* potassium *t*-butoxide in *t*-butyl alcohol. The procedure then followed was identical with that utilized in studying the elimination of alkyl bromides by potassium *t*-butoxide.²⁵

The following procedure is typical of those used for the study of the elimination reaction of the *t*-alkyl tosylates. *t*-Amyl alcohol (10.0 g., 0.113 mole) and *p*-toluenesulfonyl chloride (39 g., 0.226 mole) were dissolved in 100 ml. of dry pyridine. The reaction mixture was heated under reflux in a Todd micro column and olefin was collected as it was formed (24 hours). There was obtained a 91% yield of olefin of n_D^{20} 1.3839, corresponding to a composition of 36% 2-methyl-1-butene and 64% 2-methyl-2-butene.

A solution of 10.0 g. of *t*-amyl alcohol and 19.5 g. of *p*-toluenesulfonyl chloride in 50 ml. of dry benzene was heated

under reflux for 10 hours in a Todd micro column, as described above. No olefin was formed under these conditions.

Elimination Reactions of the *t*-Alkyl Chlorides.—The dehydrogenation of *t*-amyl bromide and chloride by potassium *t*-butoxide and of 2,4,4-trimethyl-2-pentyl bromide and chloride with 2,6-lutidine were carried out by the procedures previously described for the bromides.^{2b,c}

The experimental data are summarized in Table III.

Acknowledgment.—We wish to express our appreciation to Dr. M. Nakagawa and Mr. Y. Okamoto for their assistance with several of the experiments reported in this paper.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT DAVIS]

The Coordination of Polyalkylbenzenes with Silver Ion

BY N. OGIMACHI, L. J. ANDREWS AND R. M. KEEFER

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Argentation constants for a large number of polyalkylbenzenes have been obtained through a study of the variations in the solubilities of the aromatic substances in equimolar water-methanol solution with changes in the silver nitrate concentration of the medium. The stabilities of the silver ion complexes appear to be controlled by opposing electronic and steric effects of the alkyl substituents on the aromatic nucleus. The assumption that the unfavorable steric effects are minimized when silver ion is coordinated with the aromatic nucleus from a position above and between two unsubstituted ring carbons is in accord with the data. The results of studies of the effects of temperature changes on the magnitudes of the argentation constants indicate that as steric effects of the alkyl substituents become more pronounced the entropy losses accompanying the interactions become larger.

Thermodynamic constants for the formation of iodine and iodine monochloride complexes of polyalkylbenzenes in carbon tetrachloride solution have been reported recently.^{1,2} These data indicate rather clearly that when a number of bulky alkyl substituents are present on the benzene nucleus the normally favorable electronic influences of alkyl groups on complex stability are offset by an unfavorable steric situation. The results of earlier argentation studies,^{3,4} in which aqueous media were used, suggest that the formation of silver ion-alkylbenzene complexes is also subject to steric as well as electronic control by alkyl substituents. The available supporting evidence is, however, limited since the highly substituted benzenes are too insoluble in aqueous media to permit accurate evaluation of argentation constants by techniques which are appropriate for the simple alkylbenzenes.

This solubility problem has been overcome through use of an equimolar solution of water and methanol as the solvent for determination of argentation constants. This procedure was suggested by the method used by Nichols⁵ to study the coordination of silver ion with unsaturated esters and has been employed successfully by Kofahl and Lucas⁶ in studying the argentation of polycyclic aromatic hydrocarbons. Argentation constants for a large number of polyalkylbenzenes have now been evaluated. These and the heat, free energy and entropy changes accompanying certain of the interactions are reported here and are compared with similar data for the halogen-polyalkylbenzene interactions.

Experimental

Materials.—Commercial Solvents Corporation methanol was purified by the procedure of Morton and Mark.⁷ Skellysolve C (ligroin of boiling range 85–100°) was purified for use as a solvent in spectrophotometric studies by methods described previously.^{3,4}

The monoalkylbenzenes (Eastman Organic Chemicals white label grade) were washed successively with concentrated sulfuric acid, water and dilute sodium hydroxide and were dried and fractionated before use. Eastman organic chemicals *m*-xylene (b.p. 139.0–139.2°) was freed of its isomers by the procedure of Clarke and Taylor.⁸ Eastman organic chemicals durene (m.p. 79–80°) and pentamethylbenzene (m.p. 51.2–52.5°) were recrystallized from ethanol. Samples of *m*-diisopropylbenzene and 1,3,5-triisopropylbenzene were furnished by Dr. A. P. Lien of the Standard Oil Co. of Indiana. 1,2,3,4-Tetraethylbenzene, b.p. 119.4–120.1° (11 mm.), was prepared by the Jacobsen reaction⁹ from a mixture of tetraethylbenzenes which was obtained by alkylation of commercial triethylbenzene. All other hydrocarbons were purified as described in connection with earlier work on iodine monochloride complexes.² All inorganic chemicals were of reagent grade and were dried before use.

The Solubility Measurements.—Equimolar water-methanol solutions of varying concentrations of sodium and silver nitrate and of total ionic strength 0.5 were prepared and stored as described by Kofahl and Lucas.⁶ To samples of these solutions contained in 125-ml. glass stoppered erlenmeyer flasks were added 0.1–1.0 g. samples of aromatic hydrocarbon. The mixtures were shaken at room temperature for 12 hours in a constant temperature bath at 25.0° to saturate the aqueous methanolic phase with hydrocarbon. Longer shaking and rotating periods did not cause further increases in the concentrations of hydrocarbons dissolved in the aqueous methanol.

After a one-half hour settling interval a 10-ml. sample of the aqueous methanol phase was removed from each mixture, and this was added to 10 ml. of Skellysolve C contained in a glass stoppered erlenmeyer flask. To this mixture was added 150 ml. of water, and the flask was shaken for two hours. The optical density of the Skellysolve C phase was then measured on the Beckman spectrophotometer against a Skellysolve C blank at some appropriate wave length in the ultraviolet region. One extraction with Skellysolve C was sufficient to remove all of the dissolved hydrocarbon from the aqueous phase as evidenced by the fact that addi-

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(3) L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949).

(4) L. J. Andrews and R. M. Keefer, *ibid.*, **72**, 5034 (1950); **74**, 4500 (1952).

(5) P. L. Nichols, *ibid.*, **74**, 1091 (1952).

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