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Directive effects in elimination reactions

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DIRECTIVE EFFECTS

IN ELIMINATION REACTIONS

by

Donald Hope Froemsdorf

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of

The Requirements for the Degree of

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Head of Major Department

Dean of Graduate College

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Ames, Iowa

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INTRODUCTION

One of the more important reactions in organic chemistry is the elimination reaction. Elimination reactions are generally considered to be reactions in which two atoms or groups are removed from a molecule without being replaced by other atoms or groups. This occurs most commonly on adjacent carbon atoms so that a more unsaturated product is produced. This type of elimination reaction is called <u>beta</u>-elimination or 1,2-elimination.

Most of the <u>beta</u>-eliminations fall into two general categories. One is the eliminations that are intramolecular, initiated by heat and proceed by a unimolecular mechanism. The other is generally referred to as a heterolytic elimination reaction. This heterolytic elimination reaction is broken down into two mechanistic classes - unimolecular eliminations and bimolecular eliminations. The unimolecular elimination is now commonly referred to as the E1 reaction and the bimolecular elimination as the E2 reaction.

In both the intramolecular and heterolytic eliminations a leaving group X and a β-hydrogen are removed from the molecule resulting in the formation of an olefin and HX. When the leaving group X is in a secondary or tertiary position, there is a choice of β-hydrogens. For example, in the following case either hydrogen atom Ha or hydrogen

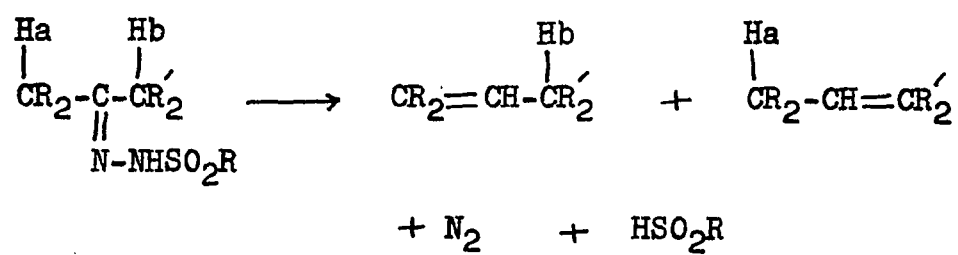$$\underset{X}{\overset{\overset{\displaystyle Ha}{\overset{\displaystyle |}{}} \overset{\displaystyle Hb}{\overset{\displaystyle |}{}}}{CR_2\text{-}CH\text{-}CR_2'}} \quad \xrightarrow{\text{-HX}} \quad \overset{\overset{\displaystyle Hb}{\overset{\displaystyle |}{}}}{CR_2\!\!=\!\!CH\text{-}CR_2'} \quad + \quad \overset{\overset{\displaystyle Ha}{\overset{\displaystyle |}{}}}{CR_2\text{-}CH\!\!=\!\!CR_2'}$$
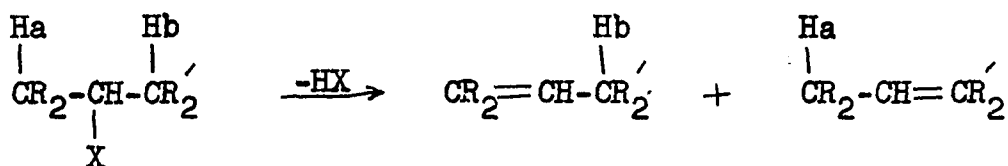
atom Hb can be removed and if R is not identical with R´, the product formed will be different, depending on which hydrogen atom is removed. This problem has been realized for more than a century, and observations have been made of the products formed with various groups X, but the underlying steric and electronic effects controlling this choice are not clear.

This thesis reports some studies on the direction of elimination in the pyrolysis of some secondary and tertiary aliphatic acetates ($X = \text{-O-CO-CH}_3$), the effect of substituents on the base-promoted elimination of 2-phenylethyl compounds by kinetic studies ($X = Br$, I, $OSO_2C_6H_4CH_3$, $\overset{+}{S}(CH_3)_2$ and $Y = \underline{p}\text{-OCH}_3$, $\underline{p}\text{-H}$, $\underline{p}\text{-Cl}$, $\underline{m}\text{-Br}$), and some prelim-

inary work on the decomposition of various aliphatic $\underline{p}$-toluenesulfonylhydrazones ($R = \text{-C}_6\text{H}_4\text{CH}_3$) in the presence
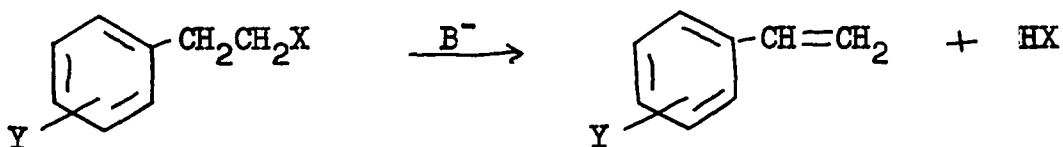
$$\underset{\underset{N-NHSO_2R}{\overset{\overset{Ha}{|}\quad\overset{Hb}{|}}{\underset{||}{CR_2-C-CR_2'}}}{} \longrightarrow \underset{\overset{Hb}{|}}{CR_2=CH-CR_2'} \quad + \quad \underset{\overset{Ha}{|}}{CR_2-CH=CR_2'}$$

$$+ \: N_2 \quad + \quad HSO_2R$$

of alkali, a reaction whose mechanism is not yet known.

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HISTORICAL

The first recorded observations of a directional preference for an elimination reaction are those of Hofmann.[1] He observed that the decomposition of a quaternary ammonium hydroxide containing an ethyl group and other primary alkyl groups yielded ethylene as the chief olefinic product.

$$(RCH_2CH_2)_3\overset{+}{N}\text{-}CH_2CH_3 + \overline{O}H \longrightarrow (RCH_2CH_2)_3N + CH_2{=\!=}CH_2$$
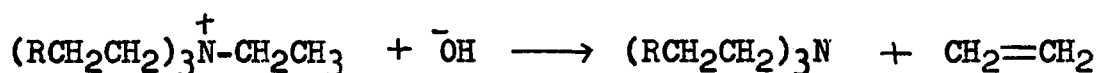
In 1875 Saytzeff[2] pointed out that the elimination of secondary and tertiary halides produced predominately the olefin in which the double bond was substituted with the largest number of alkyl groups. He concluded that the olefin formed in greatest proportion was determined by the fact that the hydrogen removed comes preferentially from the carbon atom bearing the least number of hydrogens.

$$RCH_2\underset{\overset{|}{X}}{C}HCH(CH_3)_2 \longrightarrow RCH_2CH{=\!=}C(CH_3)_2 \quad \text{major product}$$

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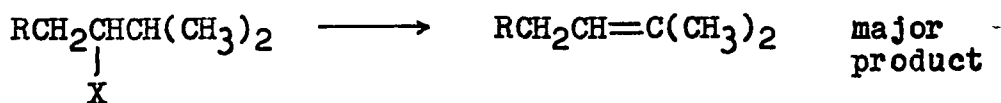
[1] A. W. Hofmann, _Ann._, _78_, 253 (1851).

[2] A. Saytzeff, _ibid._, _179_, 296 (1875).

$$RCH_2CH_2C(CH_3)_2 \longrightarrow RCH_2CH{=}C(CH_3)_2 \quad \text{major product}$$
$$\overset{|}{X}$$
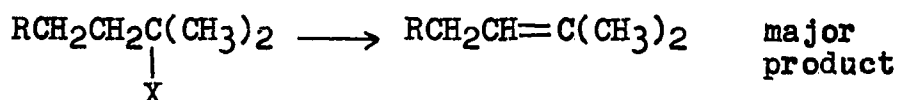
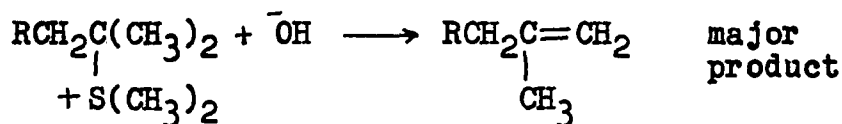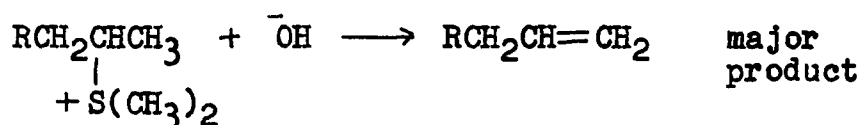These first observations have been generalized and are now known as the Hofmann and Saytzeff rules respectively. The Hofmann rule has been shown by Ingold[3] to apply to 'onium ions ($-\overset{+}{N}R_3$, $-\overset{+}{S}R_2$, $-\overset{+}{P}R_3$) in general. Ingold[3] also further extended the rule and showed that it could be applied to secondary and tertiary 'onium ions. The Hofmann rule is

$$RCH_2\overset{|}{\underset{+S(CH_3)_2}{C}HCH_3} + {}^-OH \longrightarrow RCH_2CH{=}CH_2 \quad \text{major product}$$

$$RCH_2\overset{|}{\underset{+S(CH_3)_2}{C}(CH_3)_2} + {}^-OH \longrightarrow RCH_2\overset{|}{\underset{CH_3}{C}}{=}CH_2 \quad \text{major product}$$

now generally summarized in the following way. In the elimination of 'onium salts the predominating olefinic product is the olefin that has the least number of alkyl groups attached to the double bond. The Saytzeff rule states that in the elimination of neutral-leaving groups the predominating olefinic product is the olefin that has the largest
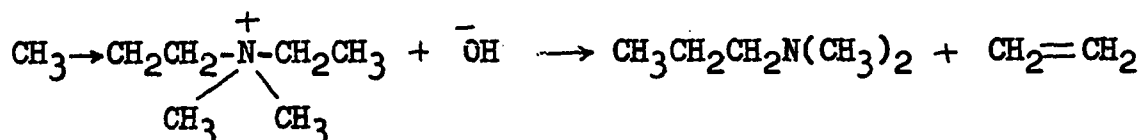
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[3]C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., p. 420 (1953).

number of alkyl groups attached to the double bond. The
scope, limitations and interpretations of these rules have
been elaborated largely by Hughes and Ingold.[3,4] A brief
summary of their views will be recorded here.

In the Hofmann elimination their view is that the
direction of elimination is determined by the acidity of
the β-hydrogen, the most acidic being removed preferential-
ly. Thus, in the decomposition of dimethylethyl-n-propyl-
ammonium hydroxide the β-hydrogens of the ethyl group would
be the most acidic. This is true because the induced
positive charge at the methylene group is partially can-
celled by electron release from the attached methyl group
(inductive effect). Thus, ethylene would be predicted,
and is, the predominating olefin produced. By the same

$$CH_3 \rightarrow CH_2CH_2 - \overset{+}{N} - CH_2CH_3 + \overset{-}{OH} \longrightarrow CH_3CH_2CH_2N(CH_3)_2 + CH_2 = CH_2$$
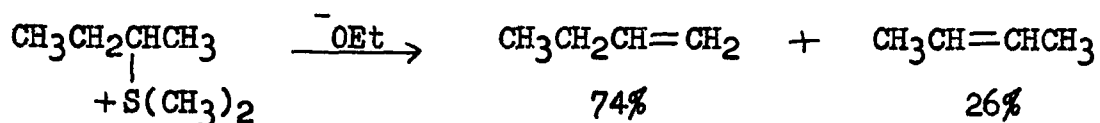$$\underset{CH_3 \quad CH_3}{}$$

reasoning the elimination of 2-butyldimethylsulfonium ion
would be expected to give a mixture of butenes with 1-
butene being the major product (the methyl hydrogens are
more acidic than the methylene hydrogens). The elimination
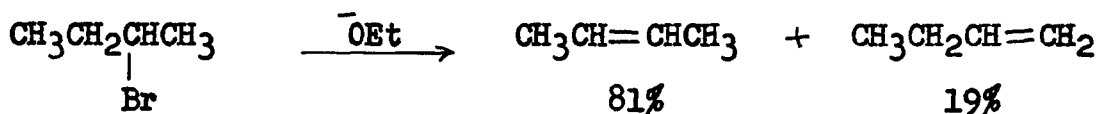of 2-butyldimethylsulfonium ion does, in fact, give 74%

[4]E. D. Hughes and C. K. Ingold, Trans. Faraday Soc.,
37, 657 (1941).

1-butene on elimination.[3]

$$CH_3CH_2\underset{\underset{+\bar{S}(CH_3)_2}{|}}{C}HCH_3 \xrightarrow{\ ^-OEt\ } CH_3CH_2CH{=}CH_2 \ + \ CH_3CH{=}CHCH_3$$
$$\qquad\qquad\qquad\qquad\qquad\quad 74\% \qquad\qquad\quad 26\%$$

The Saytzeff rule is interpreted in terms of the stability of the resulting olefinic product, the most stable olefin being formed in the greatest amount. Thus, in the elimination of 2-bromobutane the olefin formed in the greatest proportion should be 2-butene since it is more stable than 1-butene by about 2 kcal/mole.[5] The base-promoted elimination of 2-bromobutane does give 2-butene as the major product.[3] Likewise, the elimination of t-

$$CH_3CH_2\underset{\underset{Br}{|}}{C}HCH_3 \xrightarrow{\ ^-OEt\ } CH_3CH{=}CHCH_3 \ + \ CH_3CH_2CH{=}CH_2$$
$$\qquad\qquad\qquad\qquad\qquad\quad 81\% \qquad\qquad\quad 19\%$$

amyl bromide would be expected to give predominately 2-methyl-2-butene since it is more stable than the isomeric 2-methyl-1-butene by about 1.5 kcal/mole.[5] And indeed, 2-methyl-2-butene is the predominate product.[3]

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[5]C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., p. 114 (1953).

$$CH_3CH_2C(CH_3)_2 \quad \xrightarrow{\ \overline{O}Et\ } \quad CH_3CH=\underset{CH_3}{\underset{|}{C}}-CH_3 \quad + \quad CH_3CH_2\underset{CH_3}{\underset{|}{C}}=CH_2$$
$$\underset{Br}{\underset{|}{}}$$

$$71\% \qquad\qquad 29\%$$
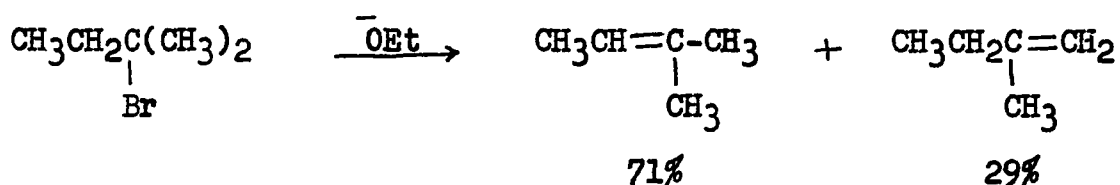
Investigations by Hughes and Ingold[3,4] have shown the Hofmann rule to be limited to the E2 reaction (bimolecular elimination), while the Saytzeff rule applys to most systems in the E1 (unimolecular elimination) and to neutral systems undergoing the E2 reaction. This is easily rationalized when we look at the mechanism of the two reactions. The E2 reaction proceeds by a bimolecular concerted process[3,4,6,7] in which the preferred stereochemistry of the β-hydrogen and the leaving group is <u>trans</u>. Thus, the leaving group
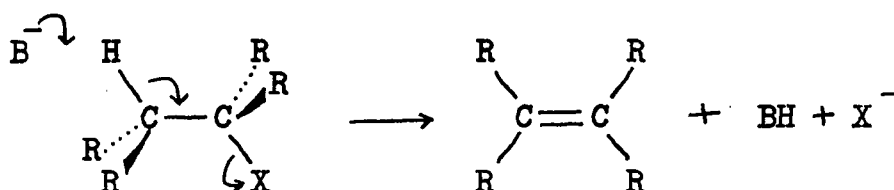

would be expected to exert some influence on the direction
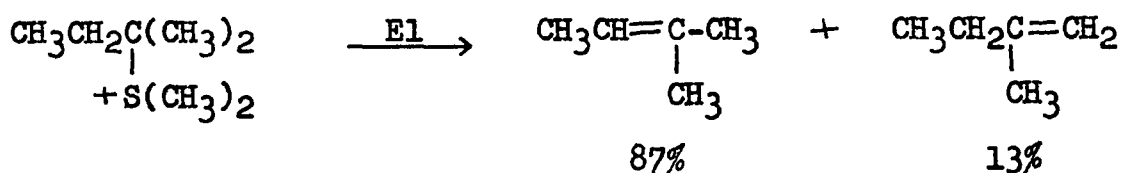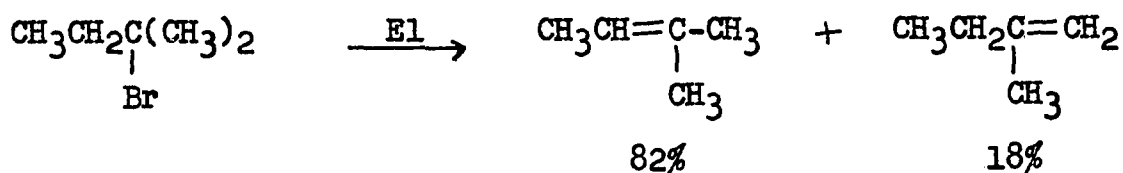
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[6]D. J. Cram, "Olefin Forming Elimination Reactions." In M. S. Newman, ed., "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., p. 305 (1956).

[7]J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., p. 168 (1956).

of elimination. On the other hand, the E1 reaction proceeds by a multistage process involving a carbonium ion as an intermediate.[3,4,6,7] Therefore, the direction of elimination

$$H-CR_2-CR_2-X \longrightarrow H-CR_2-\overset{+}{C}R_2 + X^-$$

$$H-CR_2-\overset{+}{C}R_2 \longrightarrow R_2C=CR_2 + H^+$$
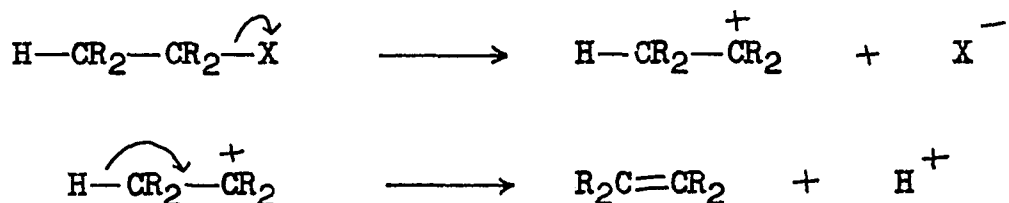
would not be expected to be influenced by the leaving group. The proton is lost from the same species (carbonium ion) regardless of the type of leaving group involved in the ionization step. The correspondence to this prediction is unmistakable in the unimolecular eliminations of t-amyl bromide[3] and t-amyldimethylsulfonium ion,[3] the olefin proportions being very nearly identical.

$$CH_3CH_2\underset{Br}{\overset{|}{C}}(CH_3)_2 \xrightarrow{E1} CH_3CH=\underset{CH_3}{\overset{|}{C}}-CH_3 + CH_3CH_2\underset{CH_3}{\overset{|}{C}}=CH_2$$

$$82\% \qquad\qquad 18\%$$

$$CH_3CH_2\underset{+S(CH_3)_2}{\overset{|}{C}}(CH_3)_2 \xrightarrow{E1} CH_3CH=\underset{CH_3}{\overset{|}{C}}-CH_3 + CH_3CH_2\underset{CH_3}{\overset{|}{C}}=CH_2$$

$$87\% \qquad\qquad 13\%$$

Brown and Moritani[8] have shown that steric factors are also important in determining the direction of elimination. They found that the unimolecular elimination of _t_-amyl chloride gave Saytzeff elimination whereas dimethylneopentyl-carbinyl chloride gave Hofmann elimination. Brown and

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \quad \xrightarrow{\text{El}} \quad CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{C}=CH_2 \quad + \quad CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=\overset{\overset{CH_3}{|}}{C}-CH_3$$

<div style="text-align:center">81%   19%</div>
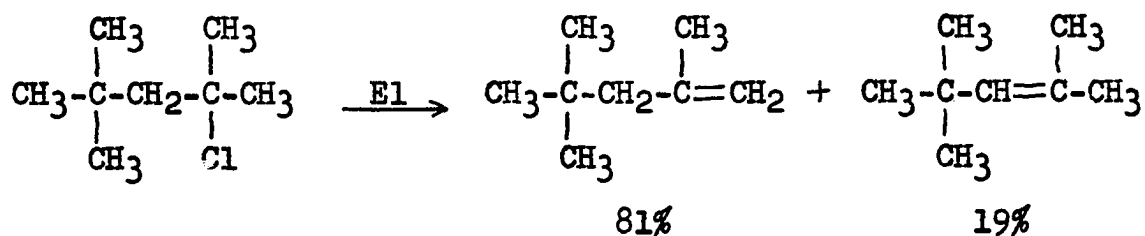
Nakagawa[9] observed a regular trend in tertiary bromides of the type

$$R-CH_2-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$
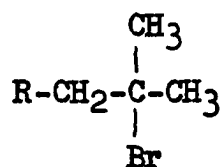
when they substituted for R methyl, ethyl, isopropyl and _t_-butyl groups respectively. The ratio of 1- to 2-olefin increased from 0.27 for R = methyl to 4.26 for R = _t_-butyl.

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[8] H. C. Brown and I. Moritani, _J. Am. Chem. Soc._, **77**, 3607 (1955).

[9] H. C. Brown and M. Nakagawa, _J. Am. Chem. Soc._, **77**, 3610 (1955).

Also, the ratio of _trans_ to _cis_-2-olefin increased in the
unimolecular elimination of secondary bromides[10] and _p_-
bromobenzenesulfonates[10,11] of the type

$$R-CH_2-\underset{\underset{X}{|}}{CH}-CH_3$$
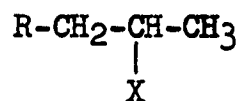
when R was made increasingly bulky. Thus, 2-pentyl _p_-
bromobenzenesulfonate gave a ratio of _trans_ to _cis_-2-olefin
of 1.4 and 4,4-dimethyl-2-pentyl _p_-bromobenzenesulfonate
gave a _trans_ to _cis_-2-olefin ratio of 83. Both of these
results appear to be due to eclipsing effects[12] in the second
stage of the El reaction. For example, in the dimethyl-
neopentylcarbinyl chloride case the transition state leading
to the Saytzeff product has a _t_-butyl and a methyl group be-
coming eclipsed, whereas in the Hofmann product a hydrogen
and a neopentyl group are becoming eclipsed. The inter-
action between the _t_-butyl and the methyl group is more un-
favorable than the interaction between the hydrogen and the
neopentyl group. On this basis the Hofmann product would be
favored. In the 4,4-dimethyl-2-pentyl _p_-bromobenzenesul-

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[10]H. C. Brown and I. Moritani, _ibid._, _77_, 3623 (1955).

[11]H. C. Brown and M. Nakagawa, _ibid._, _77_, 3614 (1955).

[12]D. Y. Curtin, _Rec. Chem. Progr._, _15_, 111 (1954).
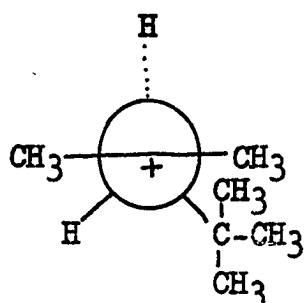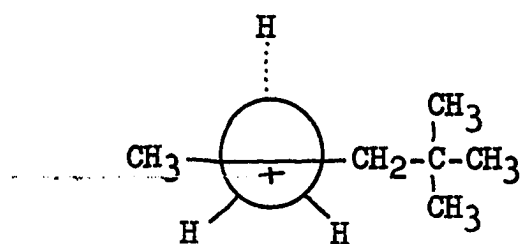
(Saytzeff)   (Hofmann)

fonate case the transition state leading to the cis-2-olefin
has a methyl and a t-butyl group becoming eclipsed, whereas
in the trans-2-olefin a hydrogen and a t-butyl group are be-
coming eclipsed. Examination of these two transition states
on the basis of eclipsing effects, predicts the trans-2-
olefin to be favored. This steric effect is apparently only
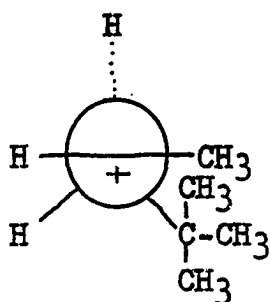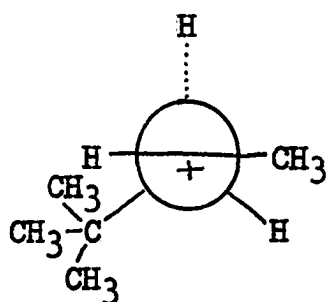
(cis olefin)   (trans olefin)

important when very bulky groups (t-butyl) are considered.
The apparent violation of the Saytzeff rule in these cases
may not actually be a violation for the so-called Hofmann
product may be the most thermodynamically stable olefinic

product.

Brown et al,[13] have studied the same series of tertiary
bromides in the E2 reaction and found that as R was varied

$$R-CH_2-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$
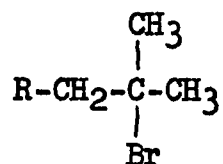
from methyl to t-butyl the ratio of 1- to 2-olefin increased
from 0.43 to 6.14 when ethoxide ion was the base and from
0.33 to 2.33 when pyridine was the base. It is proposed that
here, as in the E1 reaction, increasing the size of R makes
the transition state leading to the 2-olefin less favored
energetically than that leading to the 1-olefin.
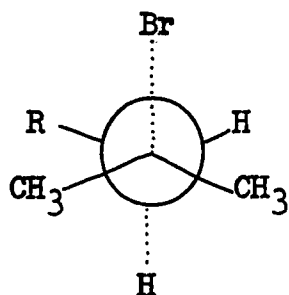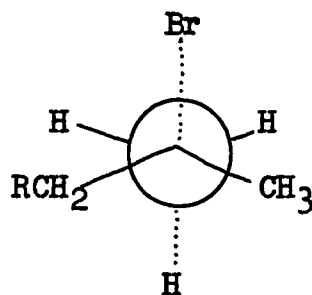
(2-olefin)   (1-olefin)

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[13]H. C. Brown, I. Moritani and M. Nakagawa, J. Am. Chem.
Soc., 78, 2190 (1956).

The effect of the size of the attacking base in the E2 reaction has also been studied by Brown and co-workers.[14,15] As the steric requirements of alkoxide and pyridine bases were increased, the amount of 1-olefin in the product in both secondary and tertiary bromides increased. Thus, t-amyl bromide gave 29% 1-olefin with ethoxide and 79% 1-olefin with t-butoxide ion.

Brown and Wheeler[16] observed that the steric requirements of the leaving group was also of importance in deter- the direction of elimination in E2 reactions. They observed that as the bulk of the leaving group increased the ratio of 1- to 2-olefin increased.

The importance of statistical factors in determining the direction of elimination should not be overlooked. The statistical factor is concerned with the availibility of hydrogens for elimination. For example, if we consider a methyl group and a methylene group, there are three hydrogens on the methyl group and two on the methylene group. Thus, there are more hydrogens available on the methyl group, and on a statistical basis only, we would predict

[14]H. C. Brown, I. Moritani and Y. Okamoto, J. Am. Chem. Soc., 78, 2193 (1956).

[15]H. C. Brown and M. Nakagawa, ibid., 78, 2197 (1956).

[16]H. C. Brown and O. H. Wheeler, ibid., 78, 2199 (1956).

that elimination would be favored in the direction of the methyl group by a factor of 3/2. The bimolecular elimination of $\underline{t}$-amyldimethylsulfonium ion[3] produces predominately 2-methyl-1-butene (Hofmann elimination). From this

$$\underset{\underset{+S(CH_3)_2}{|}}{\overset{\overset{CH_3}{|}}{CH_3CH_2-\overset{|}{C}-CH_3}} \quad \xrightarrow{\quad \overline{OEt}\quad} \quad \underset{86\%}{CH_3CH_2C{=}CH_2} \quad + \quad \underset{14\%}{\overset{\overset{CH_3}{|}}{CH_3CH{=}C-CH_3}}$$
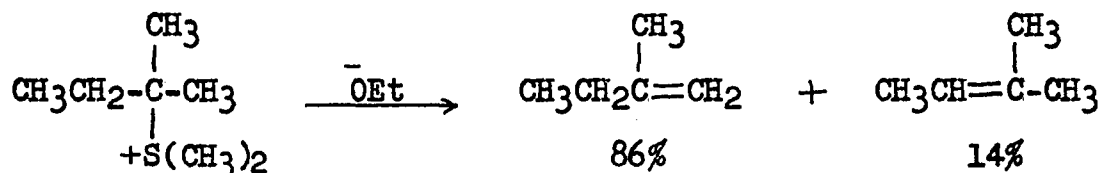
data the 1-olefin predominates by a factor of 6. However, if the availability of hydrogens is considered, we see that there are 6 hydrogens available to produce 1-olefin and 2 hydrogens available to produce 2-olefin. This gives a factor of 3 in favor of the 1-olefin. This factor of 3 divided into the observed factor of 6 results in a factor of 2 for the preference of methyl hydrogen over methylene hydrogen.

The pyrolysis of acetates is an example of an elimination reaction that is intramolecular, initiated by heat and proceeds by a unimolecular mechanism. The gross aspects of this reaction have long been recognized. Hurd and Blunck[17] proposed that the mechanism for acetate pyrolysis

[17]C. D. Hurd and F. H. Blunck, ibid., 60, 2419 (1938).

involved a cyclic intermediate in which the β-hydrogen is

hydrogen-bonded to the carbonyl oxygen of the ester. This

intermediate is not unlike what the transition state is be-

lieved to look like at the present.[6] This transition state

$$R_2C\!-\!CR_2 \qquad R_2C\!-\!CR_2 \qquad R_2C\!=\!CR_2$$

transition
state
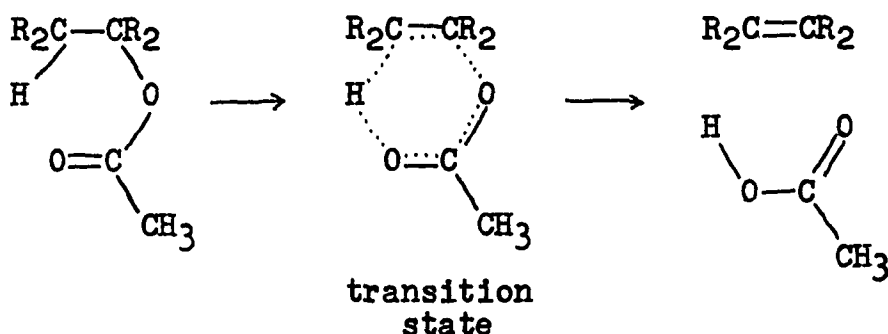
is consistent with the observed preferred cis-orientation

of the acetoxy group and the β-hydrogen eliminated,[18,19]

first order kinetics,[20,21] negative entropy of activa-

tion,[20,21] and the absence of any effect by free radical

inhibitors.

The direction of elimination in acetate pyrolysis seems

to be somewhat controversial as two apparent trends have

[18]E. R. Alexander and A. Mudrak, ibid., 72, 1810 (1950).

[19]E. R. Alexander and A. Mudrak, ibid., 72, 3194 (1950).

[20]A. T. Blades, Can. J. Chem., 32, 366 (1954).

[21]G. L. O'Connor and H. R. Nace, J. Am. Chem. Soc., 75, 2118 (1953).

been observed. Barton[22] proposed that the direction of elimination in acetate pyrolysis would be towards the most substituted carbon, thus predicting Saytzeff products. Such a directional preference was indeed observed by two groups of workers.[23,24] They observed that in the pyrolysis of (-) menthyl acetate where the acetoxy and isopropyl groups are _trans_, 35% (+) _trans-p_-menthene-2 and 65% (+) _p_-menthene-3 were formed. In contrast to these results,

65%   35%
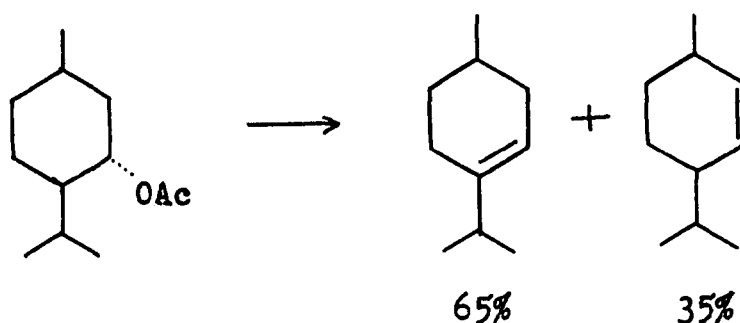
Bailey and co-workers[25,26] reported that in simple aliphatic cases the elimination proceeded in a highly selective manner, producing only that olefin predicted by the Hofmann rule.

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[22]D. H. R. Barton, _J. Chem. Soc._, 2174 (1949).

[23]J. P. Wibaut, H. C. Beyerman, and H. B. Van Leeuwen, Rec. trav. chim., _71_, 1027 (1952).

[24]W. L. McNiven and J. Read, _J. Chem. Soc._, 2067 (1952).

[25]W. J. Bailey and C. King, _J. Am. Chem. Soc._, _77_, 75 (1955).

[26]W. J. Bailey, J. J. Hewitt, and C. King, ibid., _77_, 357 (1955).

The pyrolysis of t-amyl acetate was reported to yield ex-
clusively 2-methyl-1-butene,[26] and 3-methyl-2-butyl acetate
exclusively 3-methyl-1-butene.[25]

$$CH_3CH_2\underset{\underset{OAc}{|}}{C}(CH_3)_2 \longrightarrow CH_3CH_2-\underset{\underset{CH_3}{|}}{C}=CH_2$$

>95%

$$(CH_3)_2\underset{\underset{OAc}{|}}{CHCHCH_3} \longrightarrow CH_3\underset{\underset{CH_3}{|}}{CH}-CH=CH_2$$

100%
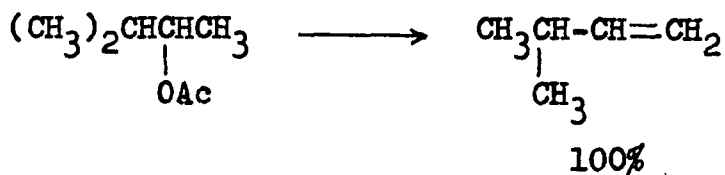
Arnold et al.[27] observed that on pyrolysis trans-2-
methylcyclohexyl acetate yielded 45% 3-methylcyclohexene
and 55% 1-methylcyclohexene. Bailey and Nicholas,[28] however,
report that the pyrolysis of trans-2-methylcyclohexyl ace-
tate yields 95% 3-methylcyclohexene and %5 1-methylcyclo-
hexene.

The pyrolysis of 1-methylcyclohexyl acetate has been
investigated and found to yield predominately (>90%) methy-

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[27]R. T. Arnold, G. G. Smith and R. M. Dodson, J. Org.
Chem., 15, 1256 (1950).

[28]W. J. Bailey and L. Nicholas, ibid., 21, 854 (1956).

lenecyclohexane by four independent workers.[25,29,30,31]

The pyrolysis of acetates with polar substituents on the β-carbon atom were also observed[32] to obey the Hofmann rule exclusively.

$$CH_3OCH_2\underset{\underset{OAc}{|}}{CH}CH_3 \longrightarrow CH_3OCH_2CH{=}CH_2$$
$$>95\%$$
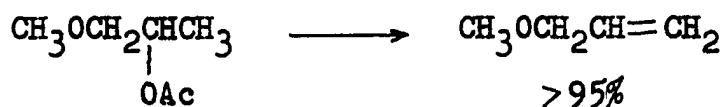
The introduction[33] of unsaturated electron-withdrawing groups in the β-position did tend to reverse the direction of elimination during pyrolysis. Thus, 1-phenyl-2-propyl acetate yielded 75% 1-phenyl-1-propene and 25% 3-phenyl-1-propene.

$$C_6H_5CH_2\underset{\underset{OAc}{|}}{CH}CH_3 \longrightarrow C_6H_5CH{=}CHCH_3 \quad + \quad C_6H_5CH_2CH{=}CH_2$$
$$75\% \qquad\qquad 25\%$$

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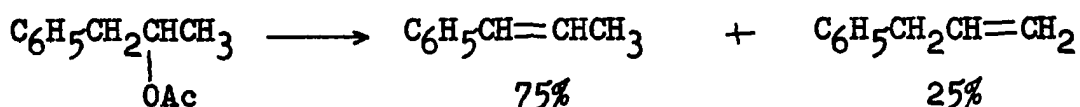
[29]T. D. Nevitt and G. S. Hammond, *J. Am. Chem. Soc.*, **76**, 4124 (1954).

[30]J. G. Trayham and O. S. Pascual, *J. Org. Chem.*, **21**, 1362 (1956).

[31]S. Siegel and M. Dunkel, Abstracts of the 129th Meeting of the American Chemical Society, p. 28N (1956).

[32]W. J. Bailey and L. Nicholas, *J. Org. Chem.*, **21**, 648 (1956).

[33]W. J. Bailey and C. King, *ibid.*, **21**, 858 (1956).

DePuy and Leary[34] studied the pyrolysis of the acetates of substituted 1,3-diphenyl-2-propanols in which the statis-

$$X-C_6H_4CH_2CHCH_2C_6H_4-Y$$
$$| $$
$$OAc$$
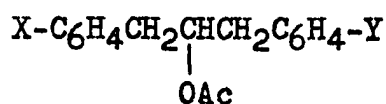
tical and steric requirements are cancelled. They found that, contrary to what would be predicted by Bailey's findings, the direction of elimination was controlled by the stability of the resulting olefin (Saytzeff rule) and that hydrogen acidity (Hofmann rule) was not important. This led them to propose that a large amount of double bond character has been developed in the transition state of acetate pyrolysis.

This review of the literature indicates there are four factors important in determining the direction of elimination, (1) hydrogen acidity, (2) thermodynamic stability of the olefinic product, (3) steric effects, and (4) the statistical availability of the hydrogens. It is also evident that the data concerning the direction of elimination in the pyrolysis of acetates were not consistent, and further, it is not possible to account for the remarkable selectivity of pyrolysis observed by Bailey by utilizing the above factors.

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[34]C. H. DePuy and R. E. Leary, J. Am. Chem. Soc., 79, 3705 (1957).

DISCUSSION

To study electronic effects in the E2 reaction, 2-
phenylethyl compounds were chosen. In this system the acid-
ity of the β-hydrogen can be changed by substitution of
various groups on the benzene nucleus. A somewhat quantita-
tive measure of the relative acidity of these hydrogens is
available from the substituent constants $(\sigma\text{-})$[35] of the sub-
stituted groups. Also the relative stability of some of the
resulting olefins is available from equilibration studies of
the olefins of the 1,3-diphenylpropyl series. Ingold and
Shoppee[36] have shown that these olefins can be equilibrated
in base. The proportions of olefins at equilibrium would be

$$Y\text{-}C_6H_4CH_2CH \quad CHC_6H_4\text{-}Z \quad \rightleftharpoons \quad Y\text{-}C_6H_4CH \quad CHCH_2C_6H_4\text{-}Z$$
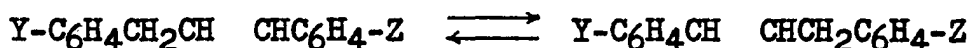
determined by their relative thermodynamic stabilities.

The leaving groups chosen for this study were bromide,
iodide, p-toluenesulfonate (hereafter to be referred to as
tosylate), and dimethylsulfonium iodides. The substituents
on the benzene nucleus were p-OCH$_3$, -H, p-Cl, and m-Br. The

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[35]L. P. Hammett, "Physical Organic Chemistry," McGraw-
Hill Book Co., New York, N. Y., p. 184 (1940).

[36]C. K. Ingold and C. W. Shoppee, *J. Chem. Soc.*, 447
(1929).

results of the elimination of these compounds in anhydrous ethanol are summarized in Table 1. The base utilized was sodium ethoxide and the reactions were run at 30.1°C.

Probably the first thing one observes in this data is that the sulfonium salts eliminate the most rapidly, whereas the tosylates are the least reactive. Also, one observes the olefin yields from all the compounds except the tosylates are essentially quantitative. This slow elimination of the tosylates is interesting since the tosylate group is apparently more reactive than bromides or iodides in displacement reactions with ethoxide ion.[37] The fact that a considerable amount of ether was formed in the tosylate reactions makes the reaction of some synthetic value since practically no substitution product was obtained with the other leaving groups.

The data in Table 1 were fitted to the Hammett equation[35] and the sensitivity of the reaction to substituents

$$\log \frac{k}{k_o} = \rho \sigma$$

determined by calculation of ρ. The values of ρ for the various leaving groups are summarized in Table 2. The conformity of the data is shown by Figure 1 and in Table 2 by

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[37]A. Streitwieser, Chem. Revs., 56, 602 (1956).

Table 1. Rates of the elimination of $YC_6H_4CH_2CH_2X$ in sodium ethoxide-ethanol solution at $30.10^\circ C$.

Y	X	10^4k	% Olefin	10^4k_{E2}
p-H	Br	4.10	100	4.10
p-Cl	Br	18.8	100	18.8
p-OCH$_3$	Br	1.73	100	1.73
m-Br	Br	37.1	100	37.1
p-H	I	26.6	100	26.6
p-Cl	I	105.	100	105.
p-OCH$_3$	I	9.56	100	9.56
m-Br	I	203.	100	203.
p-H	OTos	1.18	33	0.392
p-Cl	OTos	2.93	47	1.38
p-OCH$_3$	OTos	0.861	20	0.169
m-Br	OTos	5.53	67	3.69
p-H	$\overset{+}{S}(CH_3)_2$	37.9	100	37.9
p-Cl	$\overset{+}{S}(CH_3)_2$	218.	100	218.
p-OCH	$\overset{+}{S}(CH_3)_2$	9.13	100	9.13

observation of the standard deviations of ρ. We see that good fits to the Hammett equation were obtained with the possible exception of the p-methoxy tosylate. This con- formity of the data to the Hammett equation indicates that

hydrogen acidity is controlling the rate of reaction since

from their σ constants we know that the β-hydrogens of

Table 2. Sensitivity of the elimination of 2-phenylethyl
compounds to substituents

X	ρ [a]	log k_o [b]
OTos[c]	2.50 ± 0.06	-4.427
OTos[d]	2.04 ± 0.47	-4.280
Br	2.14 ± 0.15	-3.260
I	2.07 ± 0.09	-2.497
S(CH$_3$)$_2$	2.75 ± 0.21	-2.330

[a]Calculated by the method of least squares.

[b]Calculated intercept using ρ value given.

[c]Omitting p-methoxy point from data.

[d]Including p-methoxy point.

the m-bromo compounds are the most acidic and those of the

p-methoxy compounds the least acidic. The data further

indicates that in elimination in this system the stabili-

ty of the resulting olefin is not important. If it were,

the p-methoxystyrene should be formed more rapidly than

styrene and p-chlorostyrene less rapidly than styrene as

Figure 1. Hammett plot (log k vs σ).
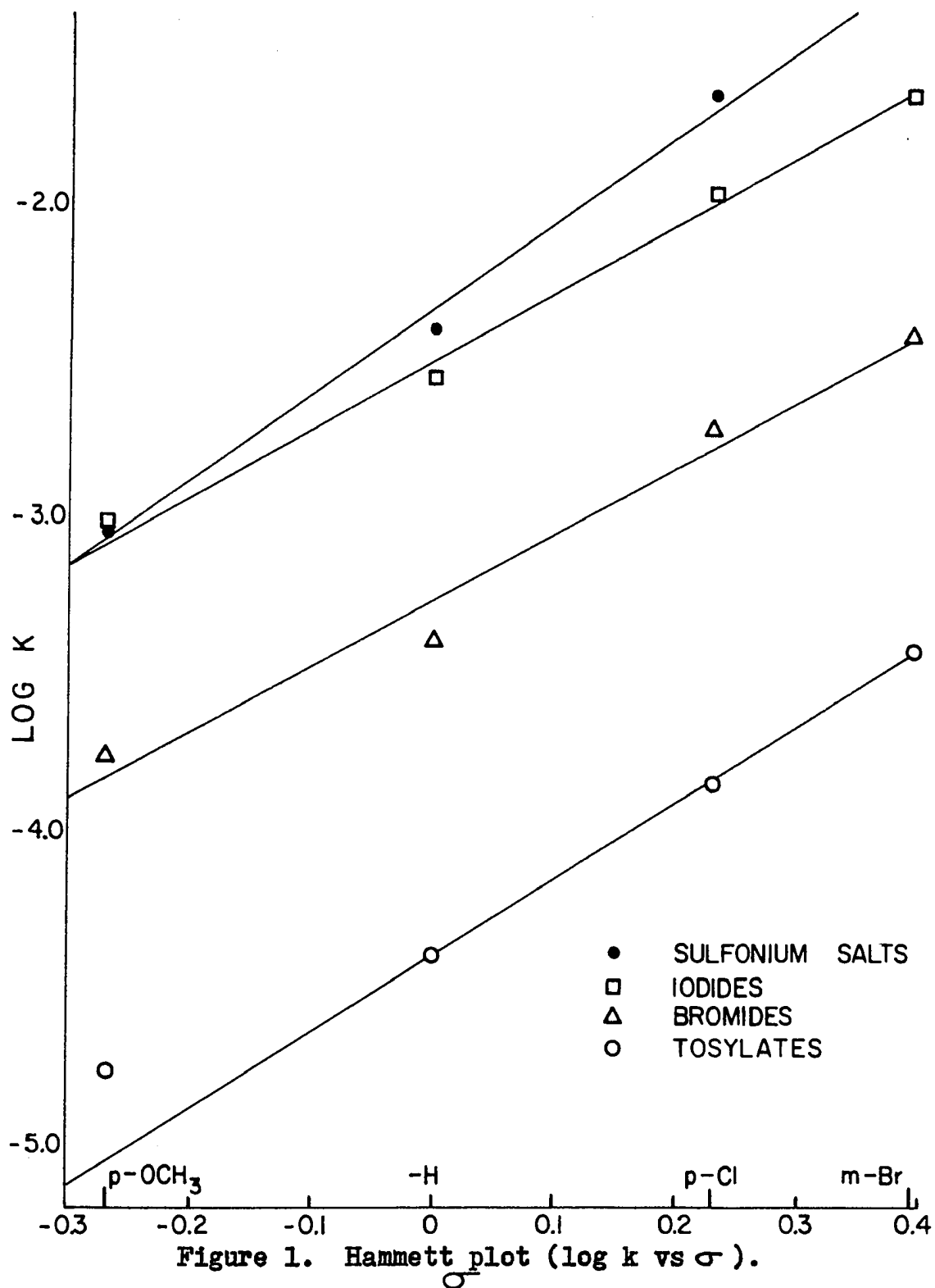
shown by the following equilibration data.[38]

$$\underline{p}\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}=\text{CHCH}_2\text{C}_6\text{H}_5 \quad \underset{\longleftarrow}{\longrightarrow} \quad \underline{p}\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}=\text{CHC}_6\text{H}_5$$
$$70\% \qquad\qquad\qquad\qquad\qquad 30\%$$

$$\underline{p}\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}=\text{CHCH}_2\text{C}_6\text{H}_4\text{Cl-}\underline{p} \quad \underset{\longleftarrow}{\longrightarrow} \quad \underline{p}\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}=\text{CHC}_6\text{H}_4\text{Cl-}\underline{p}$$
$$85\% \qquad\qquad\qquad\qquad\qquad 15\%$$
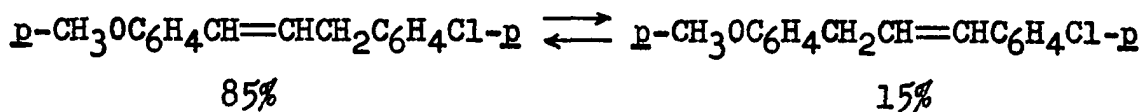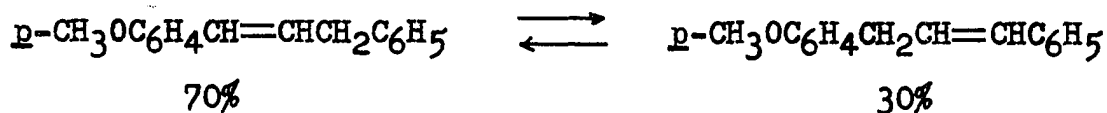
As stated before, ρ is a measure of the sensitivity of a reaction to substituents. The larger the value of ρ, the more sensitive the reaction is and the more charge is developed in the transition state. What ρ measures then is the difference in the electron density at the β-carbon atom between the ground state and the transition state. Reactions that have a large positive value for ρ have developed a large amount of negative charge in the transition state. Reactions that have a large negative value for ρ have developed a large amount of positive charge in the transition state. This then predicts that eliminations in our system have a large amount of carbanion character in the transition state.

The fact that the sulfonium salts would be the most sensitive to substituents, and the most reactive, would be

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[38] C. H. DePuy and R. E. Leary, J. Am. Chem. Soc., 79, 3705 (1957).

predicted on the basis of Ingold's[39] interpretation of the Hofmann rule. Whether the difference in the ρ values of the sulfonium salts and the bromides is enough to account for the differences in the direction of elimination ordinarily observed cannot be said with certainty. However, our data would predict that the direction of elimination of tosylates would be a case intermediate between the bromides and sulfonium salts. Examination of the literature reveals this is the result obtained in the elimination of 2-pentyl derivatives with potassium ethoxide. The bromide, tosylate, and sulfonium salt yielded 31, 48, and 87% 1-olefin respectively.[40]

The nature of the transition state of an elimination reaction is probably best discussed in terms of the following three structures.
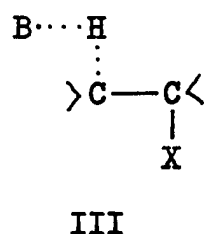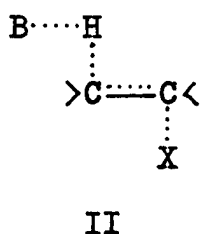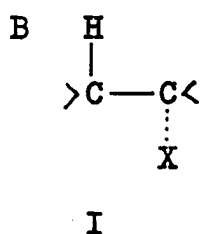
[39]C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., p. 420 (1953).

[40]H. C. Brown and O. H. Wheeler, *J. Am. Chem. Soc.*, 78, 2199 (1956).

Structure I is applicable to E1 reactions and is not pertinent to this discussion. Structure II is representative of the concerted mechanism by which simple alkyl halides are assumed to react. Structure III shows a considerable breaking of the β-carbon hydrogen bond with a resulting build up of negative charge on the β-carbon. Our results indicate that III is the best representation of the transition state in the elimination of 2-phenylethyl compounds. The fact that hydrogen acidity controls the rates of reaction in this case does not mean a contradiction of Ingold's interpretation of the Saytzeff rule.[39] By substitution of a phenyl group on the β-carbon we may have increased the acidity of the β-hydrogen sufficiently to cause a change in the transition state from II to III. Thus, product stability would not be expected to be important since there is little double bond character in the transition state. Ingold's interpretations are applicable in terms of transition state II.

The deviation of the p-methoxy tosylate is best explained in the following manner. We observed previously that by acidifying the β-hydrogen we were able to shift the transition state from II to III. Similarily if we decrease the acidity of the β-hydrogen, we should be able to cause a change in the transition state from III to II. The tosylates are the least reactive in elimination, indicating

that the tosylate group does not acidify the β-hydrogen as much as the other leaving groups. Also, we have a p-methoxy group, with a σ constant of -0.268, which is further decreasing the acidity of the β-hydrogen. Thus, of all the compounds studied the p-methoxy tosylate may have the least acidic hydrogen. If the transition state is shifted toward II, we would expect more double bond character and the stability of the p-methoxystyrene becomes important since the transition state is more like products.[41] That, indeed, this has happened is shown by the following thermodynamic data.

For 2-phenylethyl tosylate, $\Delta H^{\ddagger} = 21.0$ kcal/mole, and $\Delta S^{\ddagger} = -9.4$ e.u.; for 2-(p-methoxy)-phenylethyl tosylate, $\Delta H^{\ddagger} = 19.7$ kcal/mole, and $\Delta S^{\ddagger} = -15.4$ e.u. By examination of $\Delta H^{\ddagger}$ for the two cases one observes that the energy term for the p-methoxy tosylate is smaller, indicating other things being equal, the p-methoxy tosylate would react most rapidly. Thus, we see that the effect of the stability of the p-methoxystyrene is making itself felt. The fact that the p-methoxy tosylate does react less rapidly is due to the entropy term, since a large negative entropy increases the free energy of activation. The larger negative entropy of activation of the p-methoxy tosylate is consistant with a more ordered transition state. A more ordered transition

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[41]G. S. Hammond, _ibid._, _77_, 334 (1955).

$$\Delta F^{\ddagger} = \Delta H^{\ddagger} - T \Delta S^{\ddagger}$$

state is, of course, consistant with the change from structure III to structure II as postulated.

That the proposed change in mechanism occurs between the 2-phenylethyl tosylate and the p-methoxy tosylate is confirmed by examining the thermodynamic data of the bromides.[42] For 2-phenylethyl bromide $\Delta H^{\ddagger} = 19.6$ kcal/mole and $\Delta S^{\ddagger} = -9.2$ e.u.; for 2-(p-methoxy)-phenylethyl bromide $\Delta H^{\ddagger} = 20.8$ kcal/mole and $\Delta S^{\ddagger} = -7.3$ e.u. These data show that the difference in the rate of elimination of 2-phenylethyl tosylate and 2-phenylethyl bromide is due to differences in their heats of activation. Their nearly identical entropies of activation imply they react by the same type transition state. Their difference in rate is due then to the difference in hydrogen acidity. This difference in hydrogen acidity is due to the difference in the two leaving groups.

To test the foregoing hypothesis one should study the elimination of 2-phenylethyl tosylates with substituents that have σ constants between hydrogen and p-methoxy. A good choice would be the para and meta methyl compounds. If the

[42]W. H. Saunders, Jr., and R. A. Williams, ibid., 79, 3712 (1957).

hypothesis is correct, a trend should be observable. That is, the para and meta methyl tosylates should fall on a line between hydrogen and p-methoxy on a Hammett plot.

Further evidence for a transition state similar to III in the elimination of 2-phenylethyl compounds has been presented by Saunders and Asperger.[43] They found there was no appreciable sulfur isotope effect in the elimination of 2-phenylethyldimethylsulfonium bromide. This implies that the carbon-sulfur bond is not ruptured to any degree in the transition state, which is consistant with III and not II.

That a change in mechanism in the E2 reaction is possible by increasing the acidity of the β-hydrogen is shown by Bordwell and Kern.[44] They studied the elimination of trans-2-p-tolylsulfonylcyclohexyl tosylate with hydroxide ion. The only olefinic product they observed was 1-p-tolylsulfonylcyclohexene. Thus, in this extreme example of hydrogen

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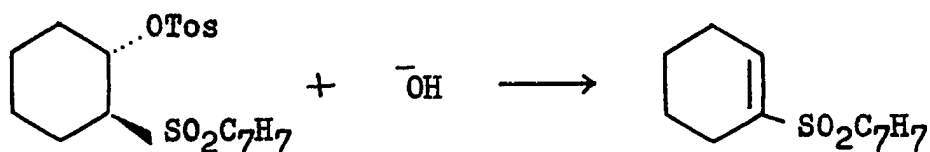
[43]W. H. Saunders, Jr., and S. Asperger, ibid., 79, 1612 (1957).

[44]F. G. Bordwell and R. J. Kern, ibid., 77, 1141 (1955).

acidity the mechanism of the E2 reaction changed so vastly that cis-elimination of an acidic hydrogen was preferred over trans-elimination of a non-acidic hydrogen. To investigate the possibility that the cis-elimination might be of approximately the same order of magnitude as the trans-elimination in the 2-phenylethyl system, trans-2-phenylcyclohexyl tosylate was reacted for 2 days with 1 N sodium ethoxide at $60^{\circ}C$. Analysis by ultraviolet spectra showed no 1-phenylcyclohexene was formed.

The inconsistancy of the data on the direction of elimination in acetate pyrolysis, as well as the inability of present theoretical concepts to explain some of the observations, prompted an examination of some simple aliphatic acetates. The first compound chosen for study was 2-butyl acetate. This choice was facilitated by the ease of product analysis by gas chromatography and the ready availability of the olefins for standardization of the chromatograph. The reaction was carried out by dropping the pure liquid ester into the top of the vertically mounted Pyrex tube which was packed with Pyrex beads. The pyrolysis tube was heated externally with an electric furnace. A slow stream of nitrogen was used to sweep the gases through the tube and the products collected in a Dry Ice trap. The result for this acetate (I) is given in Table 3.

By observation of this result one immediately notices

the wide variance from the previously observed selectivity

Table 3. Relative percentages of olefins formed in acetate
pyrolyses

	Acetate	Temp.°C.	1-Olefin	2-Olefin	1-Olefin (Calcd.)[a]
I	$CH_3CH_2CHCH_3$ | OAc	450	57	43[b]	60
II	$(CH_3)_2CHCHCH_3$ | OAc	450	80	20	75
III	$(CH_3)_2CCH_2CH_3$ | OAc	400	76	24	75
IV	$(CH_3)_2CHCH_2CHCH_3$ | OAc	500	46	54[c]	60

[a]Calculated on a statistical basis by counting the number of hydrogen available for elimination in each direction.

[b]Contained 28% _trans_ and 15% _cis_.

[c]Contained 42% _trans_ and 12% _cis_.

in simple aliphatic cases. Other secondary and tertiary

acetates were reported to yield exclusively the least highly

alkylated olefin (Hofmann rule) by Bailey and co-workers.[45,46]

The reaction was repeated several times with conversions

ranging from 69 to 99%. In each case the same result was

obtained. To show that the products were not obtained by

isomerization, n-butyl acetate was pyrolyzed under identical

conditions. In several runs only 1-butene was formed. Also,

n-butyl acetate was pyrolyzed in the presence of cis-2-

butene. The product of this pyrolysis was a mixture of 1-

butene and cis-2-butene containing no trans-2-butene, show-

ing that there was no cis-trans interconversion under the

reaction conditions.

These results prompted a reinvestigation of the esters

previously reported.[45,46] The results of some of these are

summarized in Table 3. These data are concordant and show

that the selectivity for the formation of the least highly

alkylated olefin is not nearly so great as previously indi-

cated.

In order not to overlook the possibility that there

might be conditions that would give a higher selectivity

than that observed, a series of experiments were carried out

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[45]W. J. Bailey and C. King, J. Am. Chem. Soc., 77, 75 (1955).

[46]W. J. Bailey, J. J. Hewitt, and C. King, ibid., 77, 357 (1955).

in which conditions were varied. The conversions were
varied by changing the temperature and modifying the rate
of addition of the ester. The compounds were purposely
charred. In several instances the products were recycled.
A number of runs were carried out without cleaning the
column. In all of these cases the results were consistant
within ±3%, showing that the reaction is not very sensitive
to changes in conditions.

In carrying out these reactions one cannot help but be
impressed by the cleanness of the reaction. Under ordinary
operating conditions there is no charring and colorless
products are obtained. This is a rather unexpected result
since the reactants are passed through a tube at $500^{o}C$.
Carbonization would seem to be the expected.

Probably the first thing that one observes about the
data in Table 3 is that all the olefins possible by ab-
straction of a β-hydrogen are formed. This indicates that
the direction of elimination is fairly random and the
transition states leading to these olefins do not differ
very much energetically. Of course, energy differences are
minimized by the high temperature involved. A factor of 2
difference in rate at $500^{o}C$. corresponds to a free energy
difference of about 1 kcal/mole. A free energy difference
of 1 kcal/mole corresponds to a rate difference of about 5
at room temperature.

The next thing noticeable about the data is that the Hofmann product is usually formed in the greatest amount. Also, the ratios of the olefins formed are very nearly the statistical ratio (calculated on the basis of the number of hydrogens available for elimination). For example, 2-butyl acetate produces 57% 1-butene on pyrolysis, whereas 60% 1-butene would be predicted by the ratio of methyl hydrogens to methylene hydrogens.

Closer examination of the data seems to reveal that, although there is a close agreement between the products formed and those predicted statistically, there are also electronic and steric factors operating. In these aliphatic cases the effects oppose each other and nearly cancel. Thus, the pyrolysis of 2-butyl acetate produces a 43% yield of 2-butene of which 28% is trans-2-butene and 15% is cis-2-butene. On a purely statistical basis a 50-50 mixture of cis and trans-2-butene should have been predicted. This predominance of the trans over the cis by a factor of two is probably best explained as a result of eclipsing effects. The preference for the acetoxyl group and the hydrogen eliminated to be cis,[47,48] and the proposed cyclic transition

[47]E. R. Alexander and A. Mudrak, J. Am. Chem. Soc., 72, 1810 (1950).

[48]E. R. Alexander and A. Mudrak, ibid., 72, 3194 (1950).

state[49] imply that the acetoxyl group and the hydrogen are nearly eclipsed in the transition state. The transition state leading to cis-2-butene, then, has two methyl groups almost eclipsed (Figure 2. $R = H$ and $R' = CH_3$), whereas the transition state leading to trans-2-butene has only two methyl-hydrogen interactions (Figure 2. $R = CH_3$ and $R' = H$).

$$O \cdots C-CH_3$$
$$H \quad O$$
$$R \quad R'$$
$$H \quad CH_3$$
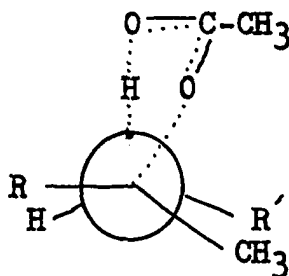
Figure 2. Transition state for acetate pyrolysis.

Certainly the methyl-methyl interactions should be less favored than the methyl-hydrogen interactions. Thus, eclipsing effects decrease the amount of 2-olefin formed by making the formation of cis-2-butene less favored energetically. The ratio of trans-2-butene to 1-butene (1 to 2) is greater than that predicted (1 to 3) for a completely random process. This deviation from the statistically predicted ratio is probably related to the stability of the resulting olefins. The difference in the heats of

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[49] C. D. Hurd and F. H. Blunck, ibid., 60, 2419 (1938).

formation of 1-butene and trans-2-butene is 2.7 kcal/mole at 25°C.[50] with trans-2-butene being more stable. Correction for statistics in this case (three methyl hydrogens versus one hydrogen leading to trans-2-butene) gives a ratio of 1 to 2/3 or 1.5 to 1. This predicts that other things being equal a methylene hydrogen is preferred over a methyl hydrogen by a factor of 1.5. Thus, the formation of 2-butene is favored by the thermodynamic stability of the resulting olefin. These two effects then, eclipsing and product stability, are opposing each other and thus tend to cancel. The statistical availability of the hydrogens remains as the predominating factor.

Similar arguments in terms of statistics, product stability, and eclipsing can be used to explain the remainder of the data. For example, consider methylisopropylcarbinyl acetate (II). In this pyrolysis 80% of 1-olefin and 20% of 2-olefin is formed. The statistical ratio would be 75% 1-olefin and 25% 2-olefin. This slight deviation is probably a manifestation of eclipsing, being somewhat more important than product stability. In t-amyl acetate (III) the actual and statistical are both 75% 1-olefin and 25% 2-olefin, the steric and thermodynamic factors exactly cancelling each

[50]C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., p. 113 (1953).

other. The methylisobutylcarbinyl case (IV) is somewhat
different than the previous cases in that the amount of 2-
olefin formed is slightly greater than the amount of 1-
olefin. However, the ratio of _trans_-2-olefin to _cis_-2-
olefin is now 3.5, as compared with a ratio of 2 in the
2-butyl acetate case (I). This result would be expected
for here the transition state leading to _cis_-4-methyl-

V
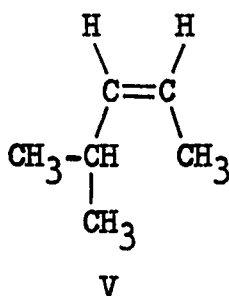
2-pentene (V) has a methyl and an isopropyl group becoming
eclipsed (Figure 2. R = H and R$'$ = -CH(CH$_3$)$_2$), which would
be less favored than the methyl-methyl interaction in the
2-butyl compound (Figure 2. R = H and R$'$ = CH$_3$). Exami-
nation of the ratio of the 1-olefin to _trans_-2-olefin shows
it has decreased from 2 in the 2-butyl case to 1.1 in this
case. This may imply that in this particular example the
thermodynamic stability of the resulting olefin is more
important than in previous compounds.

We also decided to investigate the pyrolysis of 1-
methylcyclohexyl acetate since four independent work-

ers[46,51,52,53] had claimed that Hofmann products were
formed almost exclusively. In our hands the pyrolysis of
1-methylcyclohexyl acetate always yielded 27% methylene-
cyclohexane and 73% 1-methylcyclohexene. This result

73%   27%
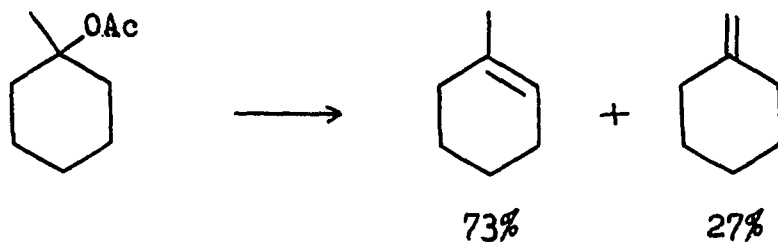
can be explained if the transition state for acetate pyroly-
sis can be formed without appreciable strain from an equa-
torial acetoxyl group and an adjacent axial hydrogen. This
implies that it is not necessary for the acetoxyl group and
the hydrogen to be exactly eclipsed in the transition state.
Exact eclipsing would mean that the ring was in the boat
form, and this would of necessity introduce many steric
factors which would favor the formation of methylenecyclo-

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[51]T. D. Nevitt and G. S. Hammond, J. Am. Chem. Soc.,
76, 4124 (1954).

[52]J. G. Traynham and O. S. Pascual, J. Org. Chem.,
21, 1362 (1956).

[53]S. Siegel and M. Dunkel, Abstracts of the 129th
Meeting of the American Chemical Society, p. 28N (1956).

hexane. The statistical availability of hydrogen in a mixed alkyl-alicyclic system such as this may not be obtained by simply counting the number of hydrogens. There are two axial hydrogens available for elimination and three methyl hydrogens. However, the ring hydrogens are rigidly held in place while the methyl hydrogens are on a freely rotating methyl group. Thus, it seems reasonable to assume only two of the methyl hydrogens are as available as the ring hydrogens, predicting a statistical exo-endo ratio of close to one. Further, free rotation of the methyl group will be lost in the formation of methylenecyclohexane while no such loss of motion occurs when a ring hydrogen is eliminated to form 1-methylcyclohexene. Finally the greater stability of the endocyclic olefin, 2.1 kcal/mole at 25°C.,[54] should favor its formation.

To investigate the effect of temperature on the ratios of products, 1-methylcyclohexyl and t-amyl acetate were pyrolyzed at various temperatures. The results of these pyrolyses are summarized in Tables 4 and 5 respectively. The remarkable consistancy of the ratios of products in these two compounds strongly implies that the ratios of products formed are not sensitive to changes in temperature.

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[54]R. B. Turner and R. H. Garner, J. Am. Chem. Soc., 79, 253 (1957).

Table 4. The effect of temperature on the pyrolysis of 1-
methylcyclohexyl acetate

Temp.°C.	% Conv.	% exo	% endo
550	90	26	74
500	--	27	73
450	94	27	73
400	69	27	73
350	46	28	72
190	0	--	--

Table 5. The effect of temperature on the pyrolysis of t-
amyl acetate

Temp.°C.	% Conv.	% 1-Olefin	% 2-Olefin
500	95	76	24
400	71	76	24
350	48	79	21
250	0	--	--

At this point a reinvestigation of the effect of polar
substituents on the β-carbon seemed necessary. The pyrolysis
of 1-methoxyisopropyl acetate had been reported, and methyl

allyl ether was claimed to be the exclusive product formed.[55] Our data would indicate the methoxyl group would exert a stabilizing influence on the transition state in the same way it stabilizes the olefin. This would predict that in comparison with the 2-butyl acetate more 2-olefin would be formed. Also, since the steric requirements of the methoxyl group are not as great as a methyl group, the ratio of trans to cis-2-olefin should be smaller. Thus, on an a priori basis a 50-50 mixture of the enol ether (VI) and methyl allyl ether (VII) would be predicted. The results obtained are in excellent agreement with these predictions.

$$CH_3OCH_2CHCH_3 \longrightarrow CH_3OCH=CHCH_3 + CH_3OCH_2CH=CH_2$$

OAc   30% trans   47%
             23% cis

             VI   VII

$$CH_3CH_2CHCH_3 \longrightarrow CH_3CH=CHCH_3 + CH_3CH_2CH=CH_2$$

OAc   28% trans   57%
             15% cis
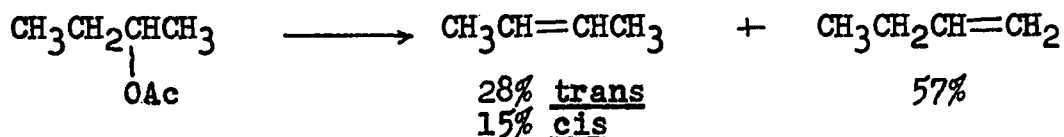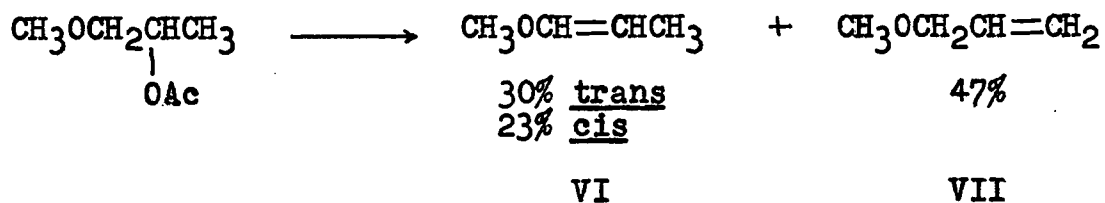
[55]W. J. Bailey and L. Nicholas, J. Org. Chem., 21, 648 (1956).

Table 6. Pyrolysis of 114 g. of 1-methylcyclohexyl
acetate[a] (effect of column conditioning)

Fraction	% exo	% endo
1	27.4	72.6
2	26.8	73.2
3	27.7	72.3
4	26.9	73.1
5	27.6	72.4
6	27.4	72.6
Average	27.3	72.7

[a]This pyrolysis was carried out at 450 C., and an over-all conversion of 94% was obtained.

The possibility that the pyrolysis column could be conditioned during a run was investigated by pyrolyzing 114 g. of 1-methylcyclohexyl acetate. Six fractions were collected and analyzed separately. The results of this pyrolysis are summarized in Table 6. The remarkable consistency throughout the run verifies the fact that this is apparently not a realizable factor.

Finally to investigate the breaking of the C-O bond, we did experiments to determine the relative rates of some acetates. The results of these are given in Table 7.

Table 7. Relative rates of pyrolysis of acetates at 400°C.[a]

Acetate	Relative Rate
5-Nonyl acetate	1
1-Phenylethyl acetate	0.74
2-Phenylethyl acetate	0.07
2-Acetoxycyclohexanone	0.06

[a]C. H. DePuy, R. W. King and D. H. Froemsdorf, Tetrahedron, [To be published in 6 ca. 1959].

They are consistant with the concerted mechanism. If heterolytic bond breaking were important, the rate of 2-acetoxy-cyclohexanone should have differed from that of 1-phenyl-ethyl acetate by a factor greater than ten. A positive charge adjacent to a benzene nucleus is considerable more stable than one adjacent to a carbonyl group.

This reinvestigation of the direction of elimination in acetate pyrolysis has shown that previous reports were in error. Further, the results are now concordant and can be satisfactorily explained in terms of presently accepted theories of organic chemistry. Thus, we are now able to predict with some accuracy the products formed from a particular pyrolysis.

The decomposition of p-toluenesulfonylhydrazones of some enolizable ketones have been shown to yield olefins on decomposition in alkali.[56] It was observed for example that the hydrazone of acetone produced propylene on decomposition. To study the direction of elimination in this reaction, the hydrazones of methyl ethyl ketone (VIII), methyl ispropyl ketone (IX) and methyl isobutyl ketone (X) were chosen. The yield of olefins from these compounds was about 34% of the theoretical. However, a quantitative yield of nitrogen was obtained. This would imply that the remainder of the product was the ether formed from the solvent, ethylene glycol. The hydrocarbon products from these decompositions were analyzed by gas chromatography. The results are summarized in Figure 3. In each case a small amount of product (2-8%) was saturated hydrocarbon. Of the olefins produced the one containing the most highly alkylated double bond predominated (56-70%). Thus, these eliminations follow the Saytzeff rule.

In the decomposition of methyl isopropyl ketone (IX) 12% of 2-methyl-1-butene was formed. This product must be the result of a rearrangement. To show that the product had not arisen by equilibration of the olefins during the

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[56]W. R. Bamford and T. S. Stevens, J. Chem. Soc., 4735 (1952).

$$CH_3CH_2C-CH_3 \longrightarrow CH_3CH_2CH=CH_2 + CH_3CH_2CH_2CH_3$$

$$\underset{\underset{SO_2Ar}{|}}{\overset{||}{N-NH}}$$

28%   3-8%

VIII

$$+ \quad \underset{H}{\overset{CH_3}{\diagdown}}C=C\underset{H}{\overset{CH_3}{\diagup}} \quad + \quad \underset{H}{\overset{CH_3}{\diagdown}}C=C\underset{CH_3}{\overset{H}{\diagup}}$$

28-31%   36-38%

$$(CH_3)_2CHCCH_3 \longrightarrow \underset{\underset{CH_3}{|}}{CH_3CHCH=CH_2} + \underset{\underset{CH_3}{|}}{CH_3CHCH_2CH_3}$$

$$\underset{\underset{SO_2Ar}{|}}{\overset{||}{N-NH}}$$

24%   8%

IX

$$+ \quad \underset{\underset{CH_3}{|}}{CH_2=C-CH_2CH_3} \quad + \quad \underset{\underset{CH_3}{|}}{CH_3-C=CHCH_3}$$

12%   56%

$$(CH_3)_2CHCH_2CCH_3 \longrightarrow \underset{\underset{CH_3}{|}}{CH_3CHCH_2CH=CH_2} + \underset{\underset{CH_3}{|}}{CH_3CHCH_2CH_2CH_3}$$

$$\underset{\underset{SO_2Ar}{|}}{\overset{||}{N-NH}}$$

32%   2%

X

$$+ \quad \underset{H}{\overset{\overset{CH_3}{\diagdown}}{CH_3-CH}}C=C\underset{H}{\overset{CH_3}{\diagup}} \quad + \quad \underset{H}{\overset{\overset{CH_3}{\diagdown}}{CH_3-CH}}C=C\underset{CH_3}{\overset{H}{\diagup}}$$

32%   38%
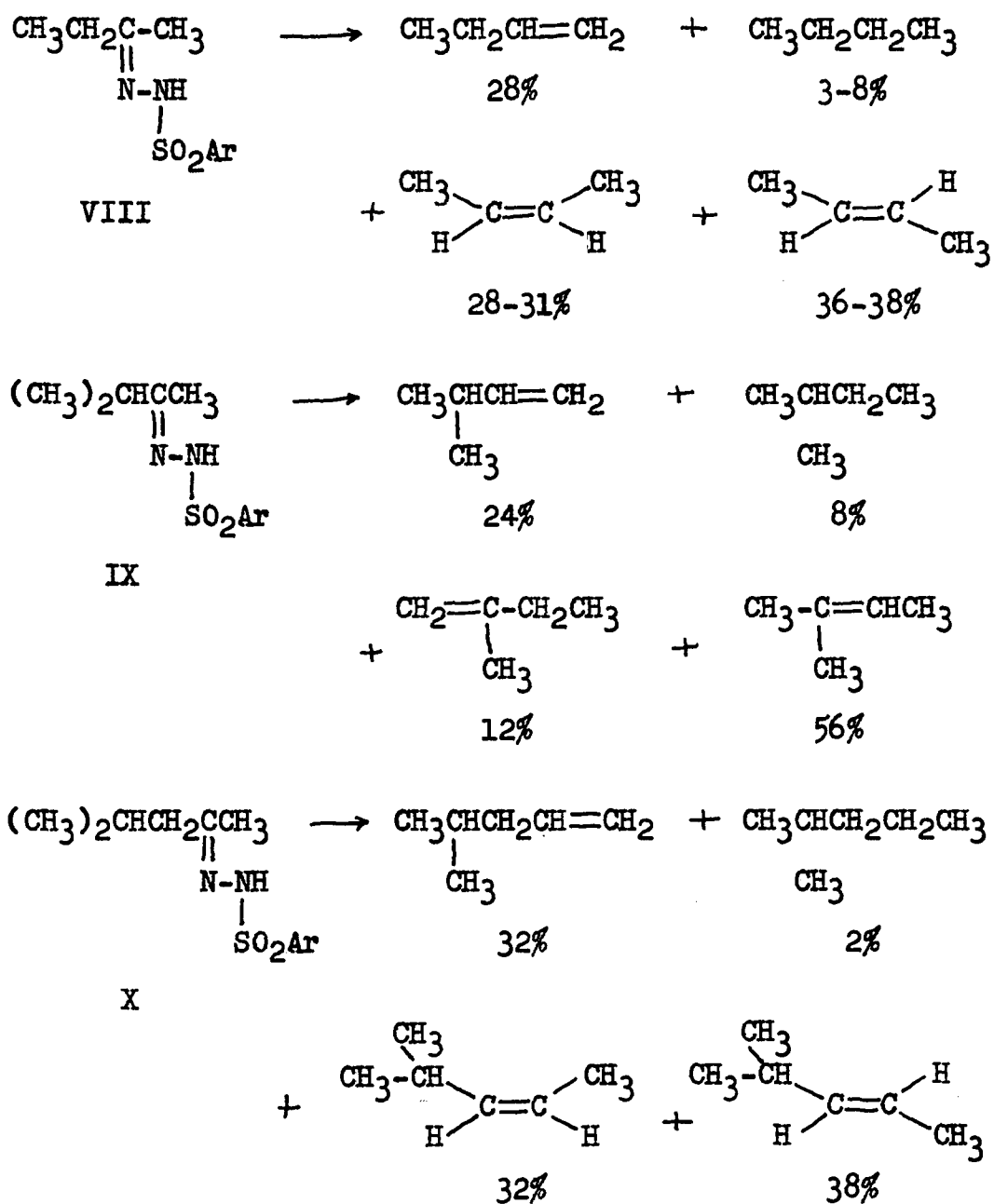
Figure 3. Products from the decomposition of p-toluene-
sulfonylhydrazones.

reaction, the pure olefins were passed through the reaction mixture under the same conditions required for decompositions. The olefins were isolated uncontaminated with rearranged products.

Similar rearrangements were observed by Bamford and Stevens.[56] Decomposition of the hydrazone of methyl t-butyl ketone (XI) yielded tetramethylethylene (XII). The
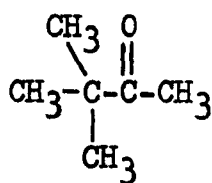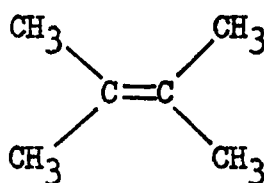
XI   XII

hydrazone of camphor (XIII) yielded camphene (XIV).
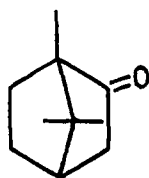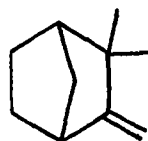
XIII   XIV

These rearrangements are best explained in terms of a carbonium ion intermediate. In addition to the observation that the reaction follows the Saytzeff rule and that products derived from rearrangement are formed, the cis-trans ratio of 2-olefins also suggests a carbonium ion inter-

mediate. The cis-trans ratio of the olefins produced from VIII and X is nearly one. The same cis-trans ratio is obtained from the acetolysis of sec-butyl tosylate.[57] This latter, being an El elimination, goes by way of an intermediate carbonium ion. The cis-trans ratio for the E2 elimination of sec-butyl bromide is 0.35.

These results indicate the sulfonylhydrazone eliminations probably proceed by way of an intermediate carbonium ion. The reaction may tentatively be formulated in the following way. A somewhat similar pathway has been

$$R_2C{=}N{-}\overset{-}{N}(SO_2C_7H_7) \xrightarrow{\ SOH\ } R_2HC{-}N{=}N{-}SO_2C_7H_7$$

olefin $\xleftarrow{-H^+}$

$$H{-}\underset{R}{\overset{R}{C}}{-}OS \xleftarrow{\ SOH\ } H{-}\underset{R}{\overset{R}{C}}{+} \quad + \quad N_2$$

rearranged products $\longleftarrow$

$$+ \quad {}^-SO_2C_7H_7$$
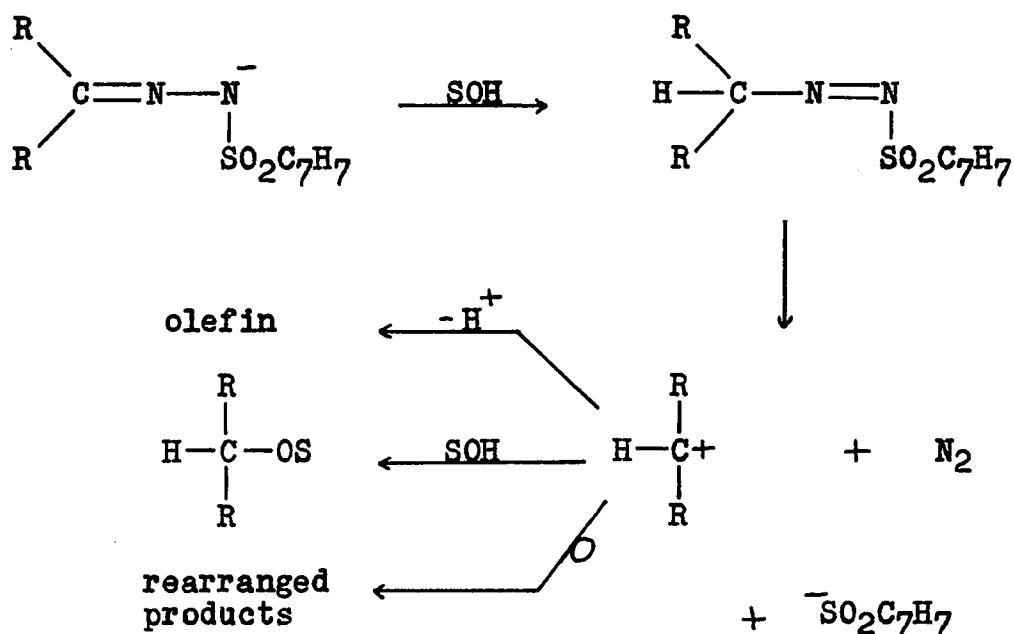
[57]H. C. Brown and M. Nakagawa, J. Am. Chem. Soc., 77, 3614 (1956).

postulated by Corey and Sneen.[58]

At the present time there is no evidence about which step is rate determining.

The saturated hydrocarbon formed may arise in either of two ways. One would be the abstraction of a hydride ion from the solvent which would simultaneously form the aldehyde derived from the solvent (ethylene glycol). A more reasonable possibility would involve a nucleophilic attack of the ethylene glycolate ion on the sulfur atom displacing the hydrazone anion. This anion would proceed in the same manner as in the Wolff-Kishner reduction. The conditions for the Wolff-Kishner reduction are very analogous and the anion displaced above is proposed to be an intermediate in this reaction.

Since we have a base present in sodium ethylene glycolate, it is not unreasonable to assume some of the olefin might be formed by a base-catalyzed elimination. This would be very analogous to what is believed to happen in the reaction of amines with nitrous acid.[59]

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[58]E. J. Corey and R. A. Sneen, J. Am. Chem. Soc., 78, 6269 (1956).

[59]A. Strietwieser, Jr., J. Org. Chem., 22, 861 (1957).

EXPERIMENTAL

Preparation and Purification of Materials

Preparation of 2-arylethyl compounds

m-Bromoacetophenone   This was prepared by the method of Pearson and Pope.[60] To 339 g. of anhydrous aluminum chloride, contained in a flask equipped with a gas outlet and drying tubes, 100 g. of acetophenone was added dropwise with stirring. When the addition of acetophenone was completed, the flask was warmed to make the mass more fluid and 134 g. of bromine was added at room temperature within 10 minutes. After being stirred an additional hour* and becoming semi-solid, the mixture was quenched in a slurry of ice and acid. The product was then extracted with ether, the ether layer washed with saturated sodium bicarbonate solution, water, and dried over anhydrous sodium sulfate. The ether was distilled and the residue fractionated, yielding 103.5 g. (61%) of m-bromoacetophenone, b.p. 91-94°C. (2 mm.) (lit.[60] b.p. 94-95°C. (2 mm.)).

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[60]D. E. Pearson and A. W. Pope, J. Org. Chem., 21, 381 (1956).

*Care must be taken at this point for if stirred too long, the mixture will solidify, making its removal from the flask very tedious.

<u>m-Bromophenylacetic acid</u>   This was prepared by the
method of Solmssen and Wenis.[61] To 103.5 g. of m-bromo-
acetophenone and 67.6 g. of morpholine, 24.9 g. of sulfur
was added. The mixture was stirred and refluxed for 15
hours. The resulting thiomorpholide was hydrolyzed by
boiling with 1.2 liters of 10% potassium hydroxide for 18
hours. The solution was then acidified, and the acid
filtered. Recrystallization from an ethanol-water mixture
yielded 78.7 g. (70.7%) of m-bromophenylacetic acid, m.p.
99-100°C. (lit.[62] m.p. 100°C.).

<u>2-(m-Bromophenyl)-ethanol</u>   To a flask equipped with
a water separator and containing 0.5 moles of m-bromo-
phenylacetic acid, 0.65 moles of benzene and 1 mole of
ethanol, 1 ml. of concentrated sulfuric acid was added. The
mixture was then refluxed for 15 hours. This yielded the
ethyl ester of m-bromophenylacetic acid, b.p. 116-120°C.
(1 mm.). Lithium aluminum hydride reduction of the ethyl
ester gave the alcohol, b.p. 107-110°C. (1 mm.).

<u>2-(p-Chlorophenyl)-ethanol</u>   In a flask[63] equipped
with condensor 158 ml. of 95% ethanol, 70 ml. of concen-

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[61]U. V. Solmssen and E. Wenis, <u>J</u>. <u>Am</u>. <u>Chem</u>. <u>Soc</u>., <u>70</u>,
4200 (1948).

[62]H. Berger, <u>J</u>. <u>prakt</u>. <u>Chem</u>., <u>133</u>, 345 (1932).

[63]H. Gilman and A. H. Blatt, "Organic Syntheses," Coll.
Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 270
(1941).

trated sulfuric acid and 100 g. of p-chlorobenzyl nitrile was
mixed. The mixture was refluxed for 7 hours. After cooling,
the mixture, which consisted of a solid and a liquid, was
poured into 343 ml. of water. The lower layer was separated
and washed with sodium bicarbonate. The product was then
distilled to give 114.8 g. (88%) of the ethyl ester, b.p.
107-112°C. (1 mm.). Lithium aluminum hydride reduction of
the ester gave 78 g. (75.5%) of the alcohol, b.p. 98-100°C.
(1 mm.) (lit.[64] b.p. 110°C. (0.5 mm.)).

2-(p-Methoxyphenyl)-ethanol   This alcohol was pre-
pared from p-methoxyacetophenone by the same method[61] as
the 2-(m-bromophenyl)-ethanol, b.p. 110-113°C. (1 mm.)
(lit.[65] b.p. 148°C. (19 mm.)).

2-Arylethyl p-toluenesulfonates   The p-toluenesul-
fonates were prepared from the corresponding alcohol by
Tipson's procedure.[66] The alcohol was dissolved in anhy-
drous pyridine and the solution cooled to -5°C. Then p-
toluenesulfonyl chloride was added with shaking until the
solid dissolved. After standing overnight, the mixture was
diluted with ice water. After the ester crystallized, it

[64]G. Baddeley and G. M. Bennett, J. Chem. Soc., 1819
(1935).

[65]G. M. Bennett and M. Hafaz, ibid., 652 (1941).

[66]R. S. Tipson, J. Org. Chem., 9, 235 (1944).

was filtered and recrystallized from an ether-pentane mixture.

2-(m-Bromophenyl)-ethyl p-toluenesulfonate, m.p. 43-44°C. Anal. Calcd. for $C_{15}H_{15}O_3SBr$: C, 50.75; H, 4.26; S, 9.02. Found: C, 51.05; H, 4.54; S, 9.44.

2-(p-Chlorophenyl)-ethyl p-toluenesulfonate, m.p. 79.3-80.3°C. Anal. Calcd. for $C_{15}H_{15}O_3SCl$: C, 58.00; H, 4.87; S, 10.32. Found: C, 58.00; H, 4.76; S, 10.69.

2-(p-Methoxyphenyl)-ethyl p-toluenesulfonate, m.p. 58.6-59.6°C. Anal. Calcd. for $C_{16}H_{18}O_4S$: C, 62.72; H, 5.92; S, 10.46. Found: C, 62.86; H, 5.82; S, 10.60.

2-Phenylethyl p-toluenesulfonate, m.p. 38.5-39°C. Anal. Calcd. for $C_{15}H_{16}O_3S$: C, 65.20; H, 5.84; S, 11.60. Found: C, 65.45; H, 5.77; S, 11.25.

2-Arylethyl bromide   The bromides were prepared by addition of the appropriate tosylate to a solution of anhydrous lithium bromide in acetone[67] and careful fractionation of the resultant bromides: 2-(m-bromophenyl)-ethyl bromide, b.p. 98-100°C. (1 mm.); 2-(p-chlorophenyl)-ethyl bromide, b.p. 79°C. (0.5 mm.); 2-(p-methoxyphenyl)-ethyl bromide, b.p. 79°C. (0.5 mm.); 2-phenylethyl bromide was Eastman Kodak Company White Label which was redistilled, b.p. 65°C. (2 mm.).

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[67]H. C. Brown and O. H. Wheeler, J. Am. Chem. Soc., 78, 2199 (1956).

2-Arylethyl iodides   The iodides were prepared by addition of the appropriate tosylate to a solution of anhydrous sodium iodide in acetone[67] and fractionation: 2-(m-bromophenyl)-ethyl iodide, b.p. 105-110°C. (1 mm.); 2-(p-chlorophenyl)-ethyl iodide, b.p. 115-117°C. (1 mm.); 2-(p-methoxyphenyl)-ethyl iodide, b.p. 117-119°C. (1 mm.): 2-phenylethyl iodide was Eastman Kodak Company White Label which was redistilled, b.p. 95°C. (3 mm.).

Sulfonium salts   The sulfonium salts were prepared by treating the appropriate iodide with sodium methyl-mercaptide[68]; this gave the sulfide. The sulfide was then treated with methyl iodide[68] in acetonitrile which gave the dimethylsulfonium iodide: 2-(p-chlorophenyl)-ethyldimethyl-sulfonium iodide, m.p. 127-128°C; 2-(p-methoxyphenyl)-ethyl-dimethylsulfonium iodide, m.p. 118-119°C; 2-phenylethyl-dimethylsulfonium iodide, m.p. 124-125°C.

Preparation of p-toluenesulfonylhydrazones

Ethyl methyl p-toluenesulfonylhydrazone was prepared[69] by the addition of ethyl methyl ketone to a solution of p-

[68]H. C. Brown and I. Moritani, J. Am. Chem. Soc., 78, 2203 (1956).

[69]W. R. Bamford and T. S. Stevens, J. Chem. Soc., 4735 (1952).

toluenesulfonylhydrazine in 1 N aqueous hydrochloric acid. The mixture was allowed to stand for 1 hour, and the product filtered and recrystallized from an ethanol-water mixture. The remainder of the hydrazones was prepared by the addition of the appropriate ketone to a solution of the hydrazine in 1% ethanolic hydrochloric acid. The mixture was refluxed for 1/2 hour and then an equal volume of water was added to the mixture, and it was kept at -10°C. overnight. The product was then filtered and recrystallized from an ethanol-water mixture.

Ethyl methyl p-toluenesulfonylhydrazone, m.p. 123-124°C.

Isopropyl methyl p-toluenesulfonylhydrazone, m.p. 121-122°C.

Isobutyl methyl p-toluenesulfonylhydrazone, m.p. 116-117°C.

Methyl neopentyl p-toluenesulfonylhydrazone, m.p. 122-123°C.

Preparation of acetates

2-Butyl acetate   Commercial (Eastman Kodak White Label) 2-Butanol was fractionated, and a center fraction was taken which had a constant boiling point of 99°C. (740 mm.)

(lit.[70] b.p. 100°C.). Analysis by gas chromatography showed
only one sharp peak. The alcohol was acetylated with pyri-
dine and acetic anhydride. The acetate was fractionated,
and a center fraction was taken which had a constant boil-
ing point of 111°C. (742 mm.) (lit.[71] b.p. 112-113°C.).
Analysis by gas chromatography showed only one sharp peak.

1-Butyl acetate   Commercial n-butyl acetate (Mathe-
son, Coleman, and Bell) was fractionated, and a center
fraction was taken which had a constant boiling point of
125°C. (740 mm.) (lit.[72] b.p. 124-125°C.). Analysis by
gas chromatography showed only one sharp peak.

3-Methyl-2-butyl acetate   3-Methyl-2-butanol was
prepared by lithium aluminum hydride reduction of methyl-
isopropyl ketone (Eastman Kodak White Label). The product
was fractionated, and the center fraction b.p. 110-111°C.
(740 mm.) (lit.[73] b.p. 111-112°C.) was collected. Analysis
by gas chromatography showed only one sharp peak. The
alcohol was acetylated with pyridine and acetic anhydride.
The acetate was fractionated, and a center fraction was taken

[70]A. T. King, ibid., 115, 1409 (1919).

[71]A. Lieben Ann., 150, 112 (1869).

[72]A. Lieben and A. Rossi, ibid., 158, 169 (1871).

[73]L. Gustus and P. G. Stevens, J. Am. Chem. Soc., 55,
385 (1933).

b.p. 127-128°C. (740 mm.) (lit.[74] b.p. 128.5-129°C.).
Analysis by gas chromatography showed only one sharp
peak.

Isoamyl acetate   Commercial isoamyl alcohol was
fractionated, and a center fraction was taken which had
a constant boiling point of 131°C. (742 mm.) (lit.[75] b.p.
132°C.). Analysis by gas chromatography showed only one
sharp peak. The alcohol was acetylated with pyridine and
acetic anhydride. The acetate was fractionated, and a
center fraction was taken, b.p. 138-139°C. (740 mm.)
(lit.[76] b.p. 142°C. (757 mm.)). Analysis by gas chromato-
graphy showed only one sharp peak.

4-Methyl-2-pentyl acetate   Commercial (Shell Chemi-
cal Co.) 4-methyl-2-pentanol was fractionated, and a center
fraction was taken which had a constant boiling point of
132°C. (742 mm.) (lit.[77] b.p. 132°C. (760 mm.)). Analysis
by gas chromatography showed only one sharp peak. The al-
cohol was acetylated with pyridine and acetic anhydride.
The acetate was fractionated, and a center fraction was
taken which had a constant boiling point of 144.5°C. (742

[74]P. G. Stevens, ibid., 55, 4237 (1933).

[75]J. V. Braun and G. Manz, Ber., 67, 1710 (1934).

[76]L. Gay, P. Mion, and M. Aumeras, Bull. Sec. Chim.,
41, 1027 (1927).

[77]R. F. Brunnel, J. Am. Chem. Soc., 45, 1334 (1923).

mm.) (lit.[78] b.p. 147-148°C.). Analysis by gas chromatography showed only one sharp peak.

t-Amyl acetate   Commercial (Sharples) t-amyl alcohol was fractionated, b.p. 100-101°C. (740 mm.) (lit.[79] b.p. 102°C.) and acetylated with dimethylaniline and acetylchloride.[80] The acetate was fractionated, b.p. 121-121.5°C. (740 mm.) (lit.[81] b.p. 124-125°C.).

2-Methyl-3-hexyl acetate   2-Methyl-3-hexanol was prepared from n-butyraldehyde and isopropylmagnesium bromide; the product was fractionated, b.p. 144-145°C. (742 mm.) (lit.[82] b.p. 144-145°C.). The alcohol was acetylated with pyridine and acetic anhydride. The acetate was fractionated, b.p. 164-164.5°C. (740 mm.) (lit.[83] b.p. 162-163°C.).

1-Methylcyclohexyl acetate   1-Methylcyclohexanol was prepared by the reaction of cyclohexanone and methylmagnesium bromide.[80] The alcohol was fractionated, b.p. 53-53.5°C. (9 mm.) (lit.[80] b.p. 68°C. (24 mm.)). The alcohol was

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[78]H. Guerbet, Compt. rend., 149, 129 (1909).

[79]R. Adams, O. Kamm, and C. S. Marvel, J. Am. Chem. Soc., 40, 1950 (1918).

[80]T. D. Nevitt and G. S. Hammond, ibid., 76, 4124 (1954).

[81]J. C. Munch, ibid., 48, 997 (1926).

[82]F. C. Whitmore and F. Johnston, ibid., 60, 2265 (1938).

[83]J. Muset, Bull, acad. roy. Belg classe sci., 775 (1906).

acetylated with dimethylaniline and acetylchloride.[71] The acetate was fractionated, b.p. 67.5-68°C. (14 mm.) (lit.[80] b.p. 74°C. (20 mm.)).

   Cyclohexylcarbinyl acetate   Cyclohexylmethanol (Eastman Kodak White Label) was acetylated with pyridine and acetic anhydride. The product was fractionated, b.p. 92-92.5°C. (20 mm.) (lit.[84] b.p. 195-196°C. (745 mm.)).

   β-Methoxyisopropyl acetate   This acetate was prepared by the method described by Bailey.[85] Commercial - methoxyisopropanol (Matheson, Coleman, and Bell) was refluxed with a large excess of acetic anhydride for 22 hours. The mixture was allowed to cool and carefully stirred into a cold saturated sodium bicarbonate solution. The aqueous mixture was extracted three times with ether, and the ether layer washed with water and dried over anhydrous sodium sulfate. The ether was distilled and fractionation of the crude acetate gave β-methoxyisopropyl acetate, b.p. 145-146°C. (lit.[86] b.p. 145.5-146°C.).

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[84]R. T. Arnold, J. Am. Chem. Soc., 70, 2591 (1948).

[85]W. J. Bailey and L. Nicholas, J. Org. Chem., 21, 648 (1956).

[86]A. A. Petrov. J. Gen. Chem. (USSR), 14, 1038 (1944).

<u>2-Acetoxycyclohexanone</u>   This acetate was prepared by the method of Shine and Hunt.[87] l-Acetoxycyclohexene was added to a dry solution of perbenzoic acid in methylene-chloride at 0°C. The corresponding epoxide which was formed was distilled at 13 mm. pressure and the fraction, which distilled between 90-115°C., yielded 2-acetoxycyclohexanone. Recrystallization of the product from pentane gave the acetoxy ketone, m.p. 35.5-36°C. (lit.[88] m.p. 35-36°C.); 2,4-dinitrophenylhydrazone, m.p. 168-169°C. (lit.[89] m.p. 167-168°C.).

Preparation of olefins and related materials

<u>Preparation of butenes</u>   1-Butene, <u>cis</u>-2-butene and <u>trans</u>-2-butene were prepared by the elimination of 2-bromo-butane with 1 N potassium ethoxide.* The retention times and the identification of the peaks from gas chromatography

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[87]H. J. Shine and G. E. Hunt, <u>J</u>. <u>Am</u>. <u>Chem</u>. <u>Soc</u>., <u>80</u>, 2434 (1958).

[88]J. Szmuszkovics and H. Born, <u>ibid</u>., <u>75</u>, 3350 (1953).

[89]F. Ramirez and A. F. Kirby, <u>ibid</u>., <u>75</u>, 6026 (1953).

*Analysis by gas chromatography gave the following results for the E2 elimination: 20% 1-butene, 21% <u>cis</u>-2-butene, and 59% <u>trans</u>-2-butene.

were assigned from the area under the peaks.[90,91] 1-Butene
was also prepared by the pyrolysis of n-butyl acetate and
the elimination of 1-bromobutane with 1 N potassium t-
butoxide.

Preparation of pentenes   3-Methyl-1-butene was pre-
pared by the pyrolysis of 3-methyl-1-butanol, acetate and
by the elimination of 3-methyl-1-bromobutane with 1 N po-
tassium t-butoxide. 2-Methyl-1-butene was prepared by the
pyrolysis of 2-methyl-1-butyl acetate. 2-Methyl-2-butene
was prepared by the dehydration of 3-methyl-2-butanol.

Preparation of hexenes   4-Methylpentene-1 and 4-
methylpentene-2 were prepared by the dehydration of 4-methyl-
2-pentanol. The retention times and the identification of
the peaks from gas chromatography were assigned on the basis
of the areas under the peaks.[92]

The heptenes   No authentic samples of the heptenes
were prepared. The assignment of the peaks from the gas
chromatography analysis were made on the basis of boiling
points since the boiling points of the two olefins obtain-

[90]H. C. Brown and O. H. Wheeler, ibid., 78, 2200 (1956).

[91]For retention volumes of the butenes on same column
we used see: A. I. M. Keulemans, A. Kwantes, and P. Zaal,
Anal. Chim. Acta, 13, 365 (1955).

[92]A. L. Heene and A. H. Matuszak, J. Am. Chem. Soc.,
66, 1649 (1944).

ed 2-methyl-3-hexene and 2-methyl-2-hexene are widely different being 85-86°C. (760 mm.)[93] and 94.4-94.6°C. (760 mm.)[93] respectively. It was assumed that the lower boiling fraction was the first peak since this was the case in all the other analyses.

<u>1-Methylcyclohexene</u>   1-Methylcyclohexene was prepared by the iodine dehydration[94] of 1-methylcyclohexanol. A trace of methylenecyclohexane was also observed in the gas chromatography analysis. Its infra-red spectra supported its structure.

<u>Methylenecyclohexane</u>   Methylenecyclohexane was prepared by the pyrolysis of cyclohexylcarbinyl acetate. The infra-red spectra which is very different from that of 1-methylcyclohexene supported its structure.

<u>Methyl allyl ether</u>   Methyl allyl ether was prepared by the dropwise addition of 34 g. of allyl bromide to a solution of 250 ml. of absolute methanol in which 7.5 g. of sodium had been dissolved. The mixture was heated at reflux for 1 hour. The product was then distilled from the reaction flask. Fractionation yielded methyl allyl ether, b.p. 42.5-43°C. (lit.[95] 42.5-43°C.).

[93]F. V. Soday and C. E. Boord, <u>ibid</u>., <u>55</u>, 3293 (1933).

[94]W. A. Mosher, <u>ibid</u>., <u>62</u>, 562 (1940).

[95]J. Irvine, J. MacDonald, and C. Soutar, <u>J</u>. <u>Chem</u>. <u>Soc</u>., <u>107</u>, 351 (1915).

<u>3-Bromo-2-methyl-1-chloropropane</u>   In a 50 ml. 3-
necked flask equipped with stirrer, reflux condenser, gas
inlet tube, and cooled in an ice bath, 35 g. of methyl allyl
chloride was placed. A slow stream of dry air was passed
through the liquid for 1/2 hour to form allyl peroxides.[96]
Then a rapid stream of hydrogen bromide (anhydrous) was
passed into the solution with stirring. A rapid stream is
required to prevent the solution from being sucked up into
the tube through which the hydrogen bromide is being added.
The hydrogen bromide was added over a period of 6 hours.
The product was then washed twice with water, quickly with
dilute sodium bicarbonate and finally with water. It was
then dried over anhydrous sodium sulfate. Distillation
yielded 47.2 g. (71%) of 3-bromo-2-methyl-1-chloropropane,
b.p. 62°C. at 25 mm.

<u>Methylcyclopropane</u>   In a 300 ml. 3-necked flask[97,98]
equipped with stirrer, dropping funnel, reflux condenser,
and connected to a dry-ice-acetone trap were placed 105 ml.
of 95% ethanol, 10.5 ml. of water, and 72 g. of Zn dust. It

[96]J. H. Brewster, <u>J</u>. <u>Am</u>. <u>Chem</u>. <u>Soc</u>., <u>73</u>, 366 (1951).

[97]R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer, and C. E. Boord, <u>ibid</u>., <u>70</u>, 946 (1948).

[98]J. T. Gragson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, <u>ibid</u>., <u>75</u>, 3344 (1953).

is necessary to maintain vigorous stirring at all times to prevent caking of the Zn. The mixture was brought to gentle reflux and 47.2 g. of 3-bromo-2-methyl-1-chloropropane was added dropwise at this temperature. Heating and stirring were continued for 23 hours although the reaction appeared to be completely over in about 3 hours. The product was then washed by bubbling it through distilled water and again collecting it in a dry-ice-acetone trap. It was then bubbled through a saturated solution of potassium permanganate to remove any olefinic materials (lit.[98] b.p. 0.7°C. (760 mm.)).

Apparatus

Gas chromatograph

The identification and determination of the relative amounts of isomeric olefins produced in the acetate pyrolysis and the decomposition of the p-toluenesulfonylhydrazones were carried out with the aid of gas chromatography. For this purpose two gas chromatographs were constructed, hereafter to be referred to as I and II respectively. A flow diagram for the gas chromatographs is shown in Figure 4.

Constant temperature air bath   Gas chromatograph I was constructed in an oven whose temperature range was from room temperature to 220°C. and the temperature could be
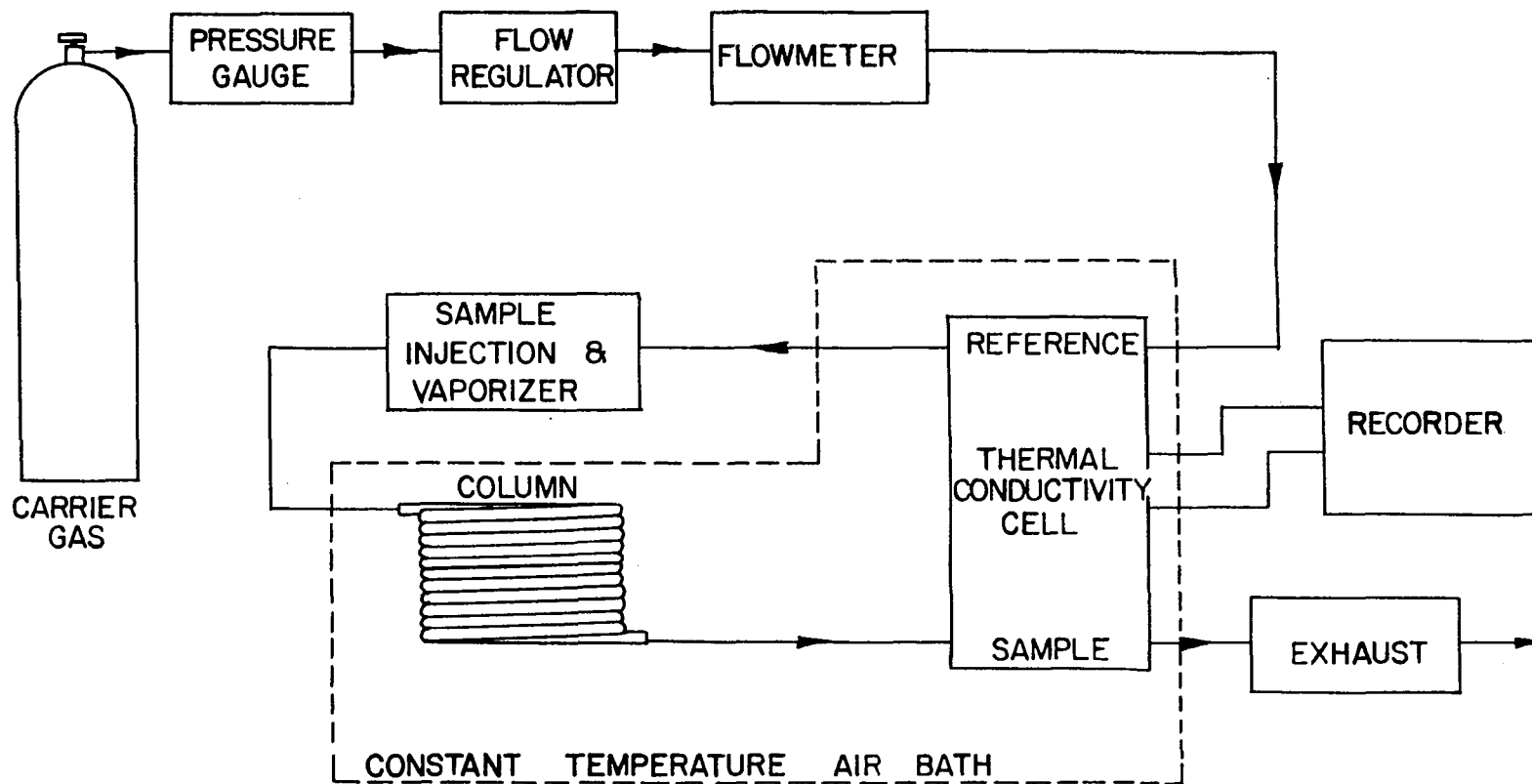
Figure 4. Flow diagram for gas chromatograph.

controlled to $\pm$ 2°C. As shown in the flow diagram, the
column and the thermal conductivity cell were enclosed in
the oven. In II both the thermal conductivity cell and the
column were enclosed in an air space provided with a vapor
jacket, a constant temperature could be maintained by re-
fluxing an appropriate liquid, although it has so far been
used only at room temperature.

Pressure gauge and flow regulator   The pressure
gauge utilized was a two stage automatic regulator. Thus,
the amount of carrier gas, helium in this case, remaining
in the tank could be readily determined and a constant head
pressure could be maintained on the column. The secondary
pressure gauge was set at 18 p.s.i.g. for I and at 4 p.s.i.g.
for II. The flow of carrier gas was regulated with the
needle valve attached to the regulator.

Flowmeter   The flowmeter for I was a rotameter pur-
chased from The Emil Greiner Company, meter number G-9142-B.
For II a simple mercury manometer was used since for a par-
ticular column the pressure differential across the column is
directly proportional to the rate of flow of the carrier gas.

Thermal conductivity cell   The detector utilized was
a thermal conductivity cell commercially available from Gow-
Mac Instrument Company, 100 Kings Road, Madison, New Jersey.
It was used without variation in I; however, in II a new
cell block was constructed, and the commercial filaments were

fitted into it. This variation was necessary because a cylindrical cell was required to fit into the vapor jacket and also it was required that the entrance and exit of the carrier gas to the reference side of the cell be on the same side of the cell block. The interior design of the cell block was identical with the commercial cell.

Sample injection and vaporizer   The introduction system for I protruded above the oven and consisted of a "T" joint in which the third side was fitted with a serum cap. It was heated with electrical heating tape. The samples were injected through the serum cap, with a hypodermic syringe, into the introduction system which was maintained at a temperature sufficiently high to vaporize the entire sample. This means that in almost all operations the introduction system was maintained at a higher temperature than the column and the detector. For II the liquid samples were either injected with a syringe or with micro dippers. The micro dippers and the introduction system constructed for their use are described by Tenney and Harris.[99] Gas samples were trapped in a length of Pyrex tubing between two stopcocks, the volume of which was 1.5 ml. The sample was then swept into the apparatus with the

[99]H. M. Tenney and R. J. Harris, Anal. Chem., 29, 317 (1957).

carrier gas.

Column   For I columns were constructed of 1/4 inch
O. D. copper tubing. The columns were packed and then
coiled so they would fit into the oven. They varied in
length from 6 to 18 feet. For II the columns were con-
structed of straight lengths of 6 mm. O. D. Pyrex glass
tubing. Columns were either 4.5 or 12.5 feet in length.
Column packings were prepared by impregnating one of many
liquid substrates such as Apiezon L stopcock grease on 40-
60 mesh firebrick or 30-50 mesh celite. For the analysis
of the butenes and the pentenes an 18-foot column of di-
butylphthalate impregnated on 40-60 mesh firebrick was used.
For the hexene analysis of 4 1/2 foot silver nitrate-
ethylene glycol column was used. The heptenes and the
cyclic olefins were analyzed on a 10-foot Apiezon L column.

Electrical circuit   The circuit diagram for the
chromatographs is shown in Figure 5. The portion enclosed
in the broken lines is the thermal conductivity cell. The
25 ohm potentiometer is used to control the filament current,
and the 1 ohm and the 100 ohm potentiometer are the coarse
and fine zero adjustments respectively. The output from
the cell is supplied with a voltage divider such that the
sensitivity of the 1 millivolt recorder used could be
changed to 1, 2, 5, 10, 20 or 50 millivolts. In all of
the wiring it was necessary to use shielded cable since
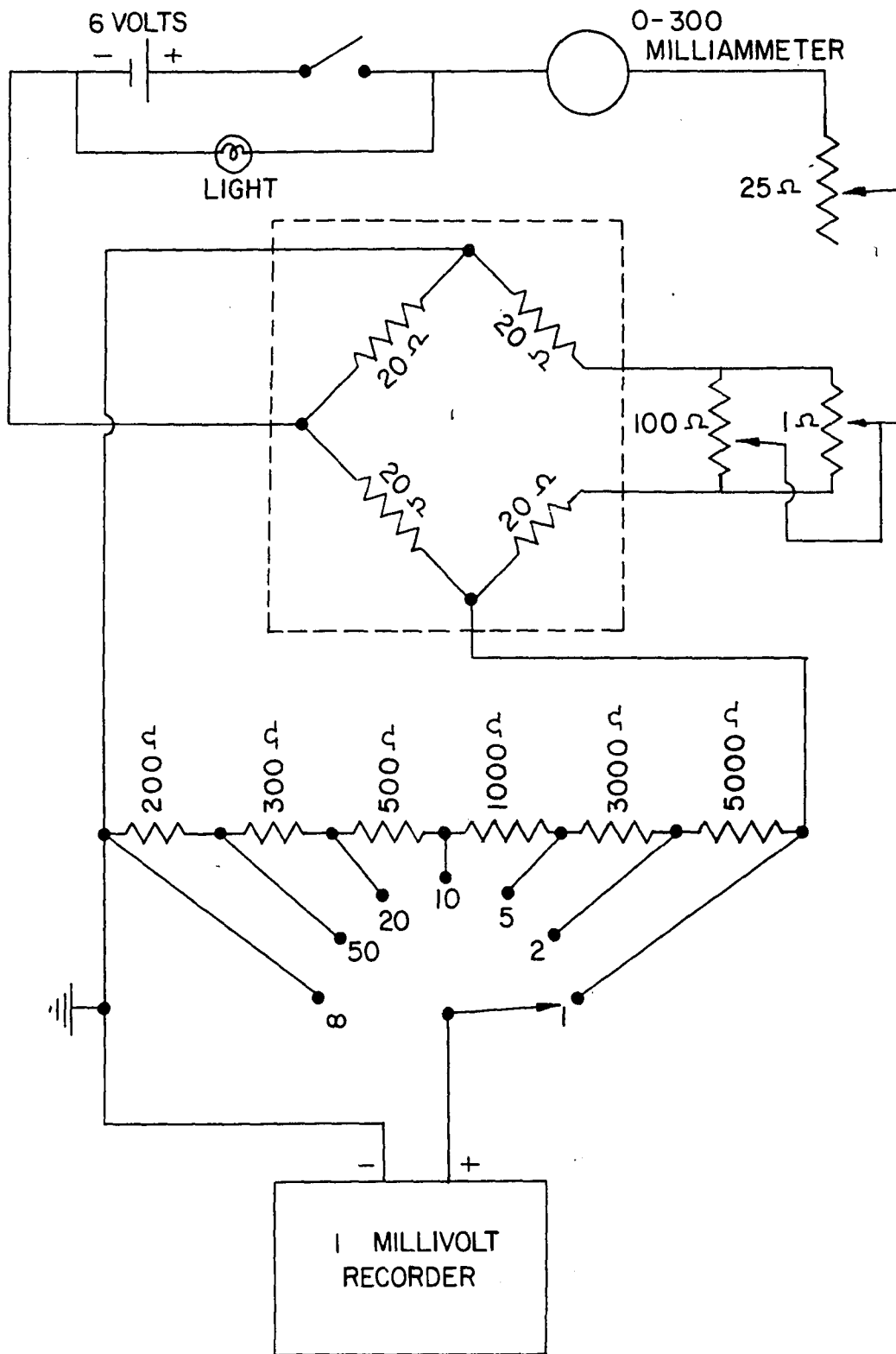
Figure 5. Circuit diagram for gas chromatograph.
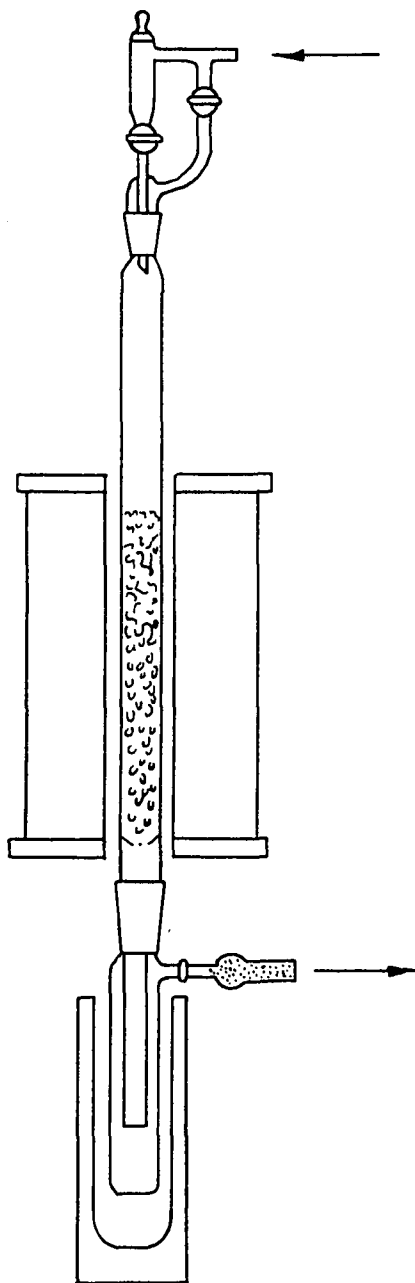
Figure 6. Pyrolysis apparatus.

ordinary wire picked up interfering external signals.

Pyrolysis apparatus

The pyrolysis apparatus is shown in Figure 6. The column was a vertically mounted 55 cm. Pyrex or Vycor tube packed with 1/8 inch Pyrex helices. The column was provided with an additional funnel for additions of the acetates and a trap to condense the pyrolysate. Heat was supplied by a 12-inch electric furnace, and the temperature was recorded by means of an Iron-Constantan thermocouple.

Procedures

Pyrolysis

Pyrolyses were carried out by dropping the liquid esters into the vertically-mounted externally-heated columns at rates of 0.5 - 7 ml. per minute. Dry, purified nitrogen was passed slowly through the columns, and the products were collected in Dry Ice traps. Then the olefinic products were either distilled into a Dry Ice trap and sampled*

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*Identical results were obtained by sampling the pyrolysate directly or distilling the olefins and sampling the olefin mixture. Consequently either technique could be used, depending upon its convenience in a particular case.

or the pyrolysis product sampled directly. The samples were then analyzed by gas chromatography. The pyrolysis column was washed with water, and the products were diluted with pentane and washed with water. An aliquot of the combined water washes was titrated with standard sodium hydroxide to determine the amount of acetic acid liberated.

Control experiments

The lack of rearrangement of olefins under the reaction conditions was demonstrated by pyrolysis of several primary acetates. In every case such reactions gave only terminal olefins. To demonstrate that no cis-trans interconversion occurred, a mixture of n-butyl acetate and cis-2-butene was passed through the column. A mixture of cis-2-butene and 1-butene, uncontaminated by trans-2-butene, was formed. In a number of cases the products of a pyrolysis were passed again through the pyrolysis column. No change in olefin ratios was observed.

Decomposition of hydrazones

One gram samples of the hydrazones were placed in 20 ml. of 1 N sodium in ethylene glycol. A slow stream of dry nitrogen was passed through the system, and the mixture

was heated to 170°C. in an oil bath. At this point de-
composition was evidenced by a vigorous evolution of nitro-
gen. The products were collected in a cold trap at -78°C.
In all cases analyses were made by gas chromatography. The
products were sampled directly, with a hypodermic syringe,
from the cold trap in which they were caught. Triplicate
analyses gave results that were within experimental error.
Mass spectral analysis was used to verify the presence of
saturated hydrocarbons as one of the products in the 2-butyl
case.

Decomposition of ethyl methyl p-toluenesulfonyl-
hydrazone in the presence of thiophenoxide ion.   One
gram of the hydrazone was placed in 20 ml. of 1 N sodium
in ethylene glycol which was 0.5 N in thiophenoxide ion.
A slow stream of dry nitrogen was passed through the system,
and the mixture was heated to 170°C. in an oil bath. The
products were collected in a cold trap at -112°C. The
yields of olefinic products obtained were calculated from
the pressure and temperature of the products in a known
volume. The yield of the olefins plus the n-butane amounted
to 34% of the theoretical.

Kinetics

The reactions were carried out in 100 ml. volumetric
flasks. About 0.006 mole of the desired compounds was placed

in the volumetric flask and weighed accurately. Then 0.12
N sodium ethoxide in absolute ethanol, previously equili-
brated thermally with the bath, was added to the calibra-
tion mark of the volumetric flask. After adequate agi-
tation, the flask was placed in the bath and allowed to
come to thermal equilibrium. Aliquots were then withdrawn
periodically with a calibrated automatic pipet. The un-
reacted base was titrated with standard acid solution.

A modification of this method was necessary for the
sulfonium salts because of their slow rate of dissolution.
The weighed sulfonium salt was dissolved in 50 ml. of ab-
solute ethanol and 0.24 N sodium ethoxide in absolute
ethanol added so the total volume was 100 ml.

The bimolecular rate constants were calculated by the
use of the integrated form of the rate equation, Equation 1.

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)} \qquad \text{(Eq. 1)}$$

The rates were calculated at different time intervals and
an average of these rates was taken as the true rate. The
data were then fitted to the Hammett equation[100], Equation 2,

[100]L. P. Hammett, "Physical Organic Chemistry," McGraw-
Hill Book Co., New York, N. Y., p. 184 (1940).

$$\log \frac{k}{k_o} = \rho\sigma \qquad \text{(Eq. 2)}$$

by the method of least squares.[101]

Styrene determinations

The reactions were allowed to go to completion, and 25 ml. aliquots were poured into water and extracted with carbon tetrachloride (3 x 10 ml.), the extract washed with water and the amount of olefin determined by bromination with standard bromide-bromate solution.[102] Duplicate runs agreed to within 1%.

In the bromination of the p-methoxystyrene it was necessary to modify the above method by adding the bromide-bromate solution in 1 ml. aliquots until a color remained to the solution. This was necessary to minimize substitution by avoiding an excess of bromine. In the case of sulfonium salts it was necessary to wash the carbon tetrachloride layer twice with saturated mercuric chloride solution to extract dimethyl sulfide.

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[101]L. P. Hammett, "Introduction to the Study of Physical Chemistry," 1st ed., McGraw-Hill Book Co., New York, N. Y., p. 410 (1952).

[102]Sidney Siggia, "Quantitative Organic Analysis via Functional Groups," 2nd ed., John Wiley and Sons. Inc., New York, N. Y., p. 68 (1954).

Results

In the decomposition of the p-toluenesulfonylhydrazones
34% yields of hydrocarbon products and quantitative yields
of nitrogen were obtained. The other 66% of the products
is presumed to be the corresponding ether formed by re-
action with sodium ethylene glycolate. The hydrocarbon pro-
ducts obtained from various hydrazones are summarized in
Table 8.

The pyrolysis of acetates yields a mixture of all the
possible olefins predictable on the basis of the available
β-hydrogens. The results for the various aliphatic acetates
considered are summarized in Table 9.

The rates of the base-promoted elimination reaction of
substituted 2-phenylethyl bromides, iodides, p-toluenesul-
fonates and dimethylsulfonium salts have been studied as a
function of substituents. The rates of reaction and amount
of elimination for a typical run for each compound are
summarized in Tables 10 through 31. Good fits to the Hammett
equation were obtained with ρ values of 2[*].

Table 8. Results of the decomposition of various p-toluenesulfonylhydrazones

Hydrazone	Products	% Yield[a]
2-butanone	n-butane	3-8
	1-butene	28
	cis-2-butene	28-31
	trans-2-butene	36-38
3-methyl-2-butanone	isopentane	8
	3-methyl-1-butene	24
	2-methyl-1-butene	12
	3-methyl-2-butene	56
4-methyl-2-pentanone	isohexane	2
	4-methyl-1-pentene	32
	cis-4-methyl-2-pentene	32
	trans-4-methyl-2-pentene	38

[a]Relative per cent yields of hydrocarbon products which amounted to 34 per cent of the theoretical.

Table 9. Results of the pyrolysis of various acetates

Acetate	Temp.°C.	% Conv.	Products		
2-Butyl	500	90	1-butene (57%) ≠ 2-butene (43%)[a]		
2-Butyl	500	91	1-butene (57%) ≠ 2-butene (43%)[a]		
2-Butyl	500	99	1-butene (57%) ≠ 2-butene (43%)[a]		
2-Butyl	450	69	1-butene (57%) ≠ 2-butene (43%)[a]		
1-Butyl	500	56	1-butene (100%)		
1-Butyl	500	80	1-butene (100%)		
3-Methyl-2-butyl	500	78	3-methyl-1-butene (80%)	≠	2-methyl-2-butene (20%)
3-Methyl-2-butyl	500	85	3-methyl-1-butene (80%)	≠	2-methyl-2-butene (20%)
3-Methyl-2-butyl	400	47	3-methyl-1-butene (80%)	≠	2-methyl-2-butene (20%)

[a]Contains 28% trans and 15% cis.

Table 9. (Continued)

Acetate	Temp.°C.	% Conv.	Products	
4-Methyl-2-pentyl	500	73	4-methyl-1-pentene (46%)[b]	≠ 4-methyl-2-pentene (54%)[b]
4-Methyl-2-pentyl	500	78	4-methyl-1-pentene (46%)[b]	≠ 4-methyl-2-pentene (54%)[b]
t-Amyl	500	95	2-methyl-1-butene (76%)	≠ 2-methyl-2-butene (24%)
t-Amyl	400	71	2-methyl-1-butene (76%)	≠ 2-methyl-2-butene (24%)
t-Amyl	400	70	2-methyl-1-butene (76%)	≠ 2-methyl-2-butene (24%)
t-Amyl	350	48	2-methyl-1-butene (79%)	≠ 2-methyl-2-butene (21%)
t-Amyl	250	0	----	----

[b]Approximate value based on peak height due to incomplete resolution.

83

Table 9. (Continued)

Acetate	Temp. °C.	% Conv.	Products	
2-Methyl-3-hexyl	450	46	2-methyl-3-hexene (73%)	≠ 2-methyl-2-hexene (27%)
2-Methyl-3-hexyl	450	41	2-methyl-3-hexene (73%)	≠ 2-methyl-2-hexene (27%)
1-Methylcyclohexyl	550	90	methylenecyclohexane (26%)	≠ 1-methylcyclohexene (74%)
1-Methylcyclohexyl	450	94	methylenecyclohexane (27%)	≠ 1-methylcyclohexene (73%)
1-Methylcyclohexyl	400	80	methylenecyclohexane (25%)	≠ 1-methylcyclohexene (75%)
1-Methylcyclohexyl	400	69	methylenecyclohexane (26%)	≠ 1-methylcyclohexene (74%)
1-Methylcyclohexyl	350	93	methylenecyclohexane (28%)	≠ 1-methylcyclohexene (72%)
1-Methylcyclohexyl	350	46	methylenecyclohexane (28%)	≠ 1-methylcyclohexene (72%)

Table 9. (Continued)

Acetate	Temp.°C.	% Conv.	Products	
1-Methylcyclohexyl	190	0	----	----
Cyclohexylcarbinyl	530	30	methylenecyclo- hexane (100%)	
1-Methoxy-2-propyl	500	57	methyl allyl ether (47%)	≠ methyl propenyl ether (53%)^c
1-Methoxy-2-propyl	515	--	methyl allyl ether (47%)	≠ methyl propenyl ether (53%)^c
2-Acetoxycyclohexanone	510	96	cyclohexenone (100%)	
2-Acetoxycyclohexanone	470	57	cyclohexenone (100%)	

^{c}Contains 30% _trans_ and 23% _cis_.

Table 10. Rate of reaction of 2-(p-methoxyphenyl)-ethyl
p-toluenesulfonate in sodium ethoxide-ethanol
solution at 54.92°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^3k (liter mole^{-1} sec.$^{-1}$)
0	5.39	----
3,000	4.76	1.00
4,260	4.33	1.43
6,120	4.20	1.20
8,040	4.04	1.13
11,400	3.70	1.26
17,580	3.50	1.10
25,080	3.24	1.26
∞	3.05	----
Rate over entire period[b]		1.20 ± .07

[a]Normality of titrant (aqueous HCl): 0.1028.
Concentration of p-toluenesulfonate: 0.0481 molar.
Concentration of sodium ethoxide: 0.1108 molar.
Five milliliter aliquots were titrated.

[b]Product contained 18% p-methoxystyrene.

Table 11. Rate of reaction of 2-phenylethyl p-toluene-sulfonate in sodium ethoxide-ethanol solution at 54.92°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^3k (liter mole^{-1} sec.$^{-1}$)
0	5.37	----
1,620	4.63	1.62
2,700	4.22	1.73
3,900	3.92	1.69
6,300	3.49	1.66
8,100	3.28	1.61
10,500	3.02	1.66
∞	2.22	----
Rate over entire period[b]		1.66 ± .03

[a]Normality of titrant (aqueous HCl): 0.1028.
Concentration of p-toluenesulfonate: 0.0648 molar.
Concentration of sodium ethoxide: 0.1104 molar.
Five milliliter aliquots were titrated.

[b]Product contained 36% styrene.

Table 12. Rate of reaction of 2-(p-methoxyphenyl)-ethyl bromide in sodium ethoxide-ethanol solution at 30.1°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$10^4 k$ (liter mole^{-1} sec.$^{-1}$)
0	5.11	----
9,000	4.79	2.03
16,800	4.73	1.32
31,440	4.42	1.49
65,460	3.94	1.63
79,380	3.81	1.18
97,980	3.68	1.69
119,400	3.56	1.70
∞	3.23	----
Rate over entire period[b]		1.58 $\pm$ .21

[a]Normality of titrant (aqueous HCl): 0.1028.
Concentration of halide: 0.0387 molar.
Concentration of sodium ethoxide: 0.1051 molar.
Five milliliter aliquots were titrated.

[b]Product contained 100% p-methoxystyrene.

Table 13. Rate of reaction of 2-(m-bromophenyl)-ethyl bromide in sodium ethoxide-ethanol solution at 30.1°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$10^3 k$ (liter mole^{-1} sec.$^{-1}$)
0	4.74	----
610	4.07	3.88
900	3.82	3.88
1,200	3.62	3.78
1,500	3.42	3.82
2,100	3.10	3.85
3,000	2.76	3.81
∞	1.23	----
Rate over entire period[b]		3.84 ± .03

[a]Normality of titrant (aqueous HCl): 0.1028.
Concentration of halide: 0.0722 molar.
Concentration of sodium ethoxide: 0.0974 molar.
Five milliliter aliquots were titrated.

[b]Product contained 100% m-bromostyrene.

Table 14. Rate of reaction of 2-(p-chlorophenyl)-ethyl bromide in sodium ethoxide-ethanol solution at 30.1°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^3k (liter mole^{-1} sec.$^{-1}$)
0	4.78	----
540	4.47	1.98
1,140	4.19	1.94
1,740	3.95	1.91
2,340	3.75	1.90
3,240	3.51	1.84
4,140	3.30	1.84
5,040	3.13	1.81
6,900	2.84	1.81
∞	1.56	----
Rate over entire period[b]		1.88 $\pm$ .05

[a]Normality of titrant (aqueous HCl): 0.1028.
Concentration of halide: 0.0662 molar.
Concentration of sodium ethoxide: 0.0982 molar.
Five milliliter aliquots were titrated.

[b]Product contained 100% p-chlorostyrene.

Table 15. Rate of reaction of 2-phenylethyl bromide in
sodium ethoxide-ethanol solution at 30.1°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^4k (liter mole^{-1} sec.$^{-1}$)
0	5.55	----
3,060	5.09	4.19
6,960	4.62	4.27
10,500	4.32	4.12
15,900	3.97	3.96
32,580	3.25	3.92
∞	2.07	----
Rate over entire period[b]		4.11 $\pm$ .12

[a]Normality of titrant (aqueous HCl): 0.1028.
Concentration of halide: 0.0716 molar.
Concentration of sodium ethoxide: 0.1141 molar.
Five milliliter aliquots were titrated.

[b]Product contained 100% styrene.

Table 16. Rate of reaction of 2-(p-methoxyphenyl)-ethyl
iodide in sodium ethoxide-ethanol solution at
30.1°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$10^4 k$ (liter mole^{-1} sec.$^{-1}$)
0	5.90	----
1,320	5.46	9.54
2,520	5.11	9.93
4,440	4.71	9.65
6,360	4.38	9.70
9,600	4.00	9.45
12,960	3.70	9.47
16,140	3.51	9.28
22,740	3.20	9.46
∞	2.64	----
Rate over entire period[b]		9.56 $\pm$ .15

[a]Normality of titrant (aqueous HCl): 0.1016.
  Concentration of halide: 0.0662 molar.
  Concentration of sodium ethoxide: 0.1199 molar.
  Five milliliter aliquots were titrated.

[b]Product contained 100% p-methoxystyrene.

Table 17. Rate of reaction of 2-(m-bromophenyl)-ethyl
iodide in sodium ethoxide-ethanol solution
at 30.1°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^2k (liter mole^{-1} sec.$^{-1}$)
0	5.22	----
90	4.83	1.89
150	4.66	1.73
210	4.54	2.59
370	4.01	2.00
600	3.63	2.03
720	3.49	2.03
840	3.38	2.02
1,020	3.24	2.04
1,200	3.16	1.98
1,500	3.03	2.04
2,100	2.88	2.03
∞	2.77	----
Rate over entire period[b]		2.03 $\pm$ .10

[a]Normality of titrant (aqueous HCl): 0.1016.
Concentration of halide: 0.0498 molar.
Concentration of sodium ethoxide: 0.1060 molar.
Five milliliter aliquots were titrated.

[b]Product contained 100% m-bromostyrene.

Table 18. Rate of reaction of 2-(p-chlorophenyl)-ethyl iodide in sodium ethoxide-ethanol solution at 30.1°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^2k (liter mole^{-1} sec.$^{-1}$)
0	5.54	----
240	4.82	1.02
480	4.30	1.05
600	4.11	1.04
720	3.92	1.06
900	3.70	1.07
1,200	3.43	1.06
1,500	3.22	1.07
2,100	2.97	1.01
∞	2.36	----
Rate over entire period[b]		1.05 ± .02

[a]Normality of titrant (aqueous HCl): 0.1016.
Concentration of halide: 0.0646 molar.
Concentration of sodium ethoxide: 0.1125 molar.
Five milliliter aliquots were titrated.

[b]Product contained 100% p-chlorostyrene.

Table 19. Rate of reaction of 2-phenylethyl iodide in
sodium ethoxide-ethanol solution at 30.1°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$10^3 k$ (liter mole^{-1} sec.$^{-1}$)
0	5.45	----
600	4.93	2.72
1,200	4.54	2.66
1,800	4.22	2.67
2,400	3.98	2.67
3,300	3.66	2.67
4,500	3.36	2.57
5,700	3.13	2.67
∞	2.18	----
Rate over entire period[b]		2.66 ± .02

[a]Normality of titrant (aqueous HCl): 0.1016.
Concentration of halide: 0.0664 molar.
Concentration of sodium ethoxide: 0.1107 molar.
Five milliliter aliquots were titrated.

[b]Product contained 100% styrene.

Table 20. Rate of reaction of 2-phenylethyl p-toluene-
sulfonate in sodium ethoxide-ethanol solution
at 30.1°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$10^4 k$ (liter mole^{-1} sec.$^{-1}$)
0	5.56	----
14,100	5.08	1.22
54,300	4.22	1.20
71,100	3.94	1.28
86,100	3.80	1.22
100,500	3.66	1.23
132,600	3.41	1.25
155,340	3.27	1.28
∞	2.71	----
Rate over entire period[b]		1.24 ± .02

[a]Normality of titrant (aqueous HCl): 0.1016.
Concentration of p-toluenesulfonate: 0.0579 molar.
Concentration of sodium ethoxide: 0.1129 molar.
Five milliliter aliquots were titrated.

[b]Product contained 100% styrene.

Table 21. Rate of reaction of 2-(p-methoxyphenyl)-ethyl p-toluenesulfonate in sodium ethoxide-ethanol solution at 30.1°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^5k (liter mole^{-1} sec.$^{-1}$)
0	5.55	----
51,300	4.63	8.38
61,500	4.47	8.76
76,200	4.34	8.39
93,600	4.16	8.56
126,120	3.89	8.82
176,100	3.62	8.88
∞	2.96	----
Rate over entire period[b]		8.63 ± .19

[a]Normality of titrant (aqueous HCl): 0.1016.
Concentration of p-toluenesulfonate: 0.0526 molar.
Concentration of sodium ethoxide: 0.1128 molar.
Five milliliter aliquots were titrated.

[b]Product contained 20% p-methoxystyrene.

Table 22. Rate of reaction of 2-(m-bromophenyl)-ethyl
p-toluenesulfonate in sodium ethoxide-ethanol
solution at 30.1°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$10^4 k$ (liter mole^{-1} sec.$^{-1}$)
0	6.21	----
3,000	5.67	5.52
7,200	5.12	5.56
10,800	4.78	5.54
14,400	4.52	5.52
18,660	4.27	5.57
30,600	3.86	5.42
37,800	3.68	5.58
45,000	3.59	5.38
∞	3.24	----
Rate over entire period[b]		5.51 ± .06

[a]Normality of titrant (aqueous HCl): 0.1016.
Concentration of p-toluenesulfonate: 0.0604 molar.
Concentration of sodium ethoxide: 0.1261 molar.
Five milliliter aliquots were titrated.

[b]Product contained 67% m-bromostyrene.

Table 23. Rate of reaction of 2-(p-chlorophenyl)-ethyl
p-toluenesulfonate in sodium ethoxide-ethanol
solution at 30.1°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^4k (liter mole^{-1} sec.$^{-1}$)
0	6.10	----
7,500	5.40	3.02
13,200	5.04	2.93
18,600	4.75	2.94
25,800	4.46	2.92
36,600	4.14	2.89
75,600	3.54	2.84
101,700	3.34	2.92
133,200	3.24	2.78
∞	3.08	----
Rate over entire period[b]		2.90 ± .05

[a]Normality of titrant (aqueous HCl): 0.1016.
Concentration of p-toluenesulfonate: 0.0614 molar.
Concentration of sodium ethoxide: 0.1239 molar.
Five milliliter aliquots were titrated.

[b]Product contained 47% p-chlorostyrene.

Table 24. Rate of reaction of 2-(p-methoxyphenyl)-ethyl-dimethylsulfonium iodide in sodium ethoxide-ethanol solution at 30.1°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$10^4 k$ (liter mole^{-1} sec.$^{-1}$)
0	5.37	----
900	5.19	9.26
2,280	4.93	9.76
3,900	4.71	9.35
7,500	4.33	9.22
11,100	4.09	8.88
17,040	3.80	8.84
24,600	3.59	8.67
∞	3.24	----
Rate over entire period[b]		9.13 ± .29

[a]Normality of titrant (aqueous HCl): 0.1016.
  Concentration of sulfonium salt: 0.0433 molar.
  Concentration of sodium ethoxide: 0.1091 molar.
  Five milliliter aliquots were titrated.

[b]Product contained 100% p-methoxystyrene.

Table 25. Rate of reaction of 2-(p-chlorophenyl)-ethyl-dimethylsulfonium iodide in sodium ethoxide-ethanol solution at 30.1°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^2k (liter mole^{-1} sec.$^{-1}$)
0	5.28	----
120	4.97	2.20
210	4.79	2.23
300	4.64	2.24
390	4.56	2.12
570	4.40	2.06
660	4.32	2.17
840	4.24	2.09
1,020	4.18	2.04
∞	3.99	----
Rate over entire period[b]		2.18 $\pm$ .09

[a]Normality of titrant (aqueous HCl): 0.1016. Concentration of sulfonium salt: 0.0264 molar. Concentration of sodium ethoxide: 0.1073 molar. Five milliliter aliquots were titrated.

[b]Product contained 100% p-chlorostyrene.

Table 26. Rate of reaction of 2-phenylethyldimethylsulfonium iodide in sodium ethoxide-ethanol solution at 30.1°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^3k (liter mole^{-1} sec.$^{-1}$)
0	5.12	----
780	4.35	4.06
1,380	3.98	3.90
2,280	3.56	3.88
2,880	3.34	3.93
3,480	3.22	3.73
4,680	2.95	3.82
6,660	2.72	3.60
8,760	2.57	3.43
∞	2.18	----
Rate over entire period[b]		3.79 ± .15

[a]Normality of titrant (aqueous HCl): 0.1016.
Concentration of sulfonium salt: 0.0597 molar.
Concentration of sodium ethoxide: 0.1040 molar.
Five milliliter aliquots were titrated.

[b]Product contained 100% styrene.

Table 27. Rate of reaction of 2-phenylethyl chloride in sodium ethoxide-ethanol solution at 30.1°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$10^6 k$ (liter mole^{-1} sec.$^{-1}$)
0	5.58	----
86,400	5.40	6.71
146,700	5.30	6.45
320,400	5.03	6.34
602,580	4.67	6.32
934,920	4.30	6.60
1,103,540	4.13	6.83
1,395,600	3.90	7.00
1,659,180	3.72	7.20
Rate over entire period		6.67 ± .25

[a]Normality of titrant (aqueous HCl): 0.1016.
 Concentration of halide: 0.0583 molar.
 Concentration of sodium ethoxide: 0.1134 molar.
 Five milliliter aliquots were titrated.

Table 28. Rate of reaction of 2-phenylethyl chloride in
potassium t-butoxide-t-butanol at 30.1°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$10^4 k$ (liter mole^{-1} sec.$^{-1}$)
0	4.52	----
10,800	3.82	2.91
20,100	3.37	3.07
27,300	3.14	3.01
37,200	2.88	2.99
68,400	2.35	3.02
79,500	2.24	3.00
∞	1.54	----
Rate over entire period[b]		3.00 ± .03

[a]Normality of titrant (aqueous HCl): 0.1016.
  Concentration of halide: 0.0606 molar.
  Concentration of potassium t-butoxide: 0.0918 molar.
  Five milliliter aliquots were titrated.

[b]Product contained 82% styrene.

Table 29. Rate of reaction of 2-phenylethyl p-toluenesulfonate in potassium t-butoxide-t-butanol at 30.1°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$10^3 k$ (liter mole^{-1} sec.$^{-1}$)
0	4.33	----
600	4.00	1.89
1,500	3.59	1.89
2,700	3.20	1.86
3,600	2.94	1.88
4,800	2.70	1.84
6,300	2.45	1.81
7,500	2.32	1.74
11,340	1.90	1.78
∞	0.72	----
Rate over entire period[b]		1.84 ± .04

[a]Normality of titrant (aqueous HCl): 0.1016.
Concentration of p-toluenesulfonate: 0.0734 molar.
Concentration of potassium t-butoxide: 0.0880 molar.
Five milliliter aliquots were titrated.

[b]Product contained 78% styrene.

Table 30. Raate of reaction of 2-phenylethyl iodide in pootassium t-butoxide-t-butanol at 30.1°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$10^2 k$ (liter mole^{-1} sec.$^{-1}$)
0	4.31	----
130	3.53	4.47
240	3.24	3.82
385	2.90	4.11
560	2.69	3.97
735	2.56	3.83
915	2.46	3.81
1,200	2.37	3.70
∞	2.22	----
Rate over enttire period[b]		3.99 $\pm$ .19

[a]Normaliity of titrant (aqueous HCl): 0.1028. Concenttration of halide: 0.0425 molar. Concenttration of potassium t-butoxide: 0.0876 molar. Five mffilliliter aliquots were titrated.

[b]Productit contained 100% styrene.

Table 31. Rate of reaction of 2-phenylethyl bromide in
potassium $\underline{t}$-butoxide-$\underline{t}$-butanol at 30.1°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$10^3 k$ (liter mole^{-1} sec.$^{-1}$)
0	4.11	----
420	3.50	7.84
840	3.08	7.94
1,260	2.80	7.75
2,220	2.38	7.49
3,120	2.14	7.32
4,260	1.94	7.18
5,160	1.83	7.10
∞	1.41	----
Rate over entire period[b]		7.52 ± .28

[a]Normality of titrant (aqueous HCl): 0.1016.
Concentration of halide: 0.0548 molar.
Concentration of potassium $\underline{t}$-butoxide: 0.0835 molar.
Five milliliter aliquots were titrated.

[b]Product contained 100% styrene.

SUMMARY

The kinetics of the base-promoted elimination of some substituted 2-phenylethyl bromides, iodides, tosylates, and sulfonium salts was studied. Good fits to the Hammett equation were obtained. The values of ρ were high ($2^\prime$), indicating a large negative charge was built up in the transition state. It was observed that hydrogen acidity was controlling the rate of reaction. A mechanism was proposed in which a considerable amount of negative charge was developed, very little double bond formation, and very little carbon heteroatom bond breaking. In one case a change in mechanism was postulated to account for the deviation of a point from the Hammett plot.

The pyrolysis of aliphatic acetates was reinvestigated, and the results of previous workers were found to be in error. The ratios of products formed were shown to be relatively insensitive to changes in temperature and other reaction conditions. Control experiments were run to show that no isomerization, either structural or geometrical, of the products occurred. The results were explained in terms of steric, thermodynamic, and statistical effects. In one instance it was shown how the ratio of products from a pyrolysis could be predicted on the basis of these effects.

Some preliminary work on the direction of elimination in the decomposition of p-toluenesulfonylhydrazones was presented. It was proposed that the elimination proceeded by way of an intermediate carbonium ion. Some evidence for this proposal was discussed.

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