

ness. The residual product gave a negative 2,4-dinitrophenylhydrazine reaction and, upon analysis by gas chromatography, was found to contain, in two runs, 46.5% and 46.0% *cis*-4-*t*-butylcyclohexanol.

Reduction of 4-*t*-Butylcyclohexanone with Diborane.—Dry diborane (from trimethylamine borane and boron fluoride)^{1b} was bubbled into a cold, rapidly stirred solution of 4-*t*-butylcyclohexanone in diglyme (under nitrogen). An acetone trap was used to catch and destroy any unreacted diborane.^{8a} The diborane addition was continued until the carbonyl absorption of the unreacted ketone had disappeared. The solution was then poured into water, extracted with pentane, dried over sodium sulfate and evaporated to dryness. Gas chromatographic analysis of the product showed 8.5% *cis*-4-*t*-butylcyclohexanol and 91.5% of the *trans*-product.

When the same reaction was effected at steam-bath temperatures, it was found that the carbonyl absorption disappeared very slowly. This was probably due to insolubility of the diborane in diglyme at this elevated temperature. The reaction was finally stopped, worked up as usual and

the unreacted ketone precipitated as the 2,4-dinitrophenylhydrazone. The filtrate was poured into water, extracted with pentane, dried and evaporated. Analysis of the residue showed it to contain 16% *cis*-4-*t*-butylcyclohexanol and 84% of the *trans* isomer.

Reduction of the 4-*t*-Butylcyclohexanone with Diborane in the Presence of BF₃.—In a typical run, equimolar amounts of 4-*t*-butylcyclohexanone (0.40 g., 2.6 millimoles) and boron fluoride ethyl ether (0.26 ml., 2.6 millimoles) were dissolved in 4.0 ml. of dry diglyme. The mixture was swept well with nitrogen and cooled in an ice-bath. Diborane was bubbled into the solution until the carbonyl absorption had disappeared. The mixture was then worked up and analyzed. It was found to contain, in two runs, 15.0 and 15.5% of the *cis*-alcohol.

Acknowledgments.—The author is indebted to Dr. G. E. Ryschkewitsch for his many helpful discussions on this work.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY]

Electronic Effects in Elimination Reactions. IV. Elimination of β -Phenylethyl Derivatives in *t*-Butyl Alcohol^{1,2}

BY C. H. DEPUY AND C. A. BISHOP

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Rates of bimolecular elimination reactions of a series of *m*- and *p*-substituted β -phenylethyl bromides, iodides and tosylates have been determined in *t*-butyl alcohol with *t*-butoxide and ethoxide as the bases. By use of the Hammett treatment it is shown that the halides undergo a more highly concerted elimination than do the tosylates. A theory is advanced to account for the low reactivity of the tosylates in this elimination, and the nature of the transition state in E₂ reactions of halides and tosylates is discussed in the light of this work and the recent work of Saunders and Edison³ on kinetic deuterium isotope effects in this system. Rho values for the SN2 reaction of β -phenylethyl tosylates with ethoxide are also reported and briefly discussed.

Recent studies on the E₂ reaction of β -phenylethyl compounds have shown that in the transition state of this bimolecular elimination reaction a great deal of carbanionic character develops on the benzyl carbon.^{4,5} Thus for a series of *m*- and *p*-substituted β -phenylethyl bromides and iodides the Hammett ρ -values^{6,7} for eliminations by ethoxide ion in ethanol were +2.1, and this value rose to +2.7 for the corresponding sulfonium salts. At the same time it was recognized that a certain amount of double-bond character was present in the transition state, for the rigid stereochemical requirements of the reaction⁸ and the sensitivity of the rate of elimination to the nature of the leaving group show that carbon-hydrogen and carbon-halogen bond breaking are highly synchronous. Although in the cases studied the acidity of the hydrogen atom being removed was very important in determining the rate of the reaction, other evidence has ac-

cumulated that the transition state in E₂ eliminations may be altered with a change in the leaving group or the base. Thus it was shown⁹ that the relative rates of the E₂ reaction of diastereomeric 1,2-diphenyl-1-propyl chlorides and bromides were a function of the base used, the stronger base giving rise to a transition state with more double bond character and hence with greater eclipsing of adjacent groups. More recently Saunders and Edison³ studied the kinetic isotope effect in the elimination of β,β -dideuterio- β -phenylethyl derivatives and showed that the extent of bond-breaking in the transition state varied with the leaving group and the strength of the base used (*vide infra*).

In an attempt to delineate more precisely the course of the reaction, and especially the timing of the bond-breaking processes, we have studied the rates of the E₂ reaction of substituted β -phenylethyl bromides, iodides and tosylates with potassium *t*-butoxide in *t*-butyl alcohol and with potassium ethoxide in *t*-butyl alcohol. It was hoped that a study of substituent effects with the stronger base would shed more light on the removal of the hydrogen and, at the same time, elucidate the reasons for the abnormally slow eliminations of the tosylates⁴ in this system. Both of these hopes have, to an extent, been realized.

The rates of the E₂ reactions for the unsubstituted, *p*-methoxy-, *p*-chloro- and *m*-bromo- β -phe-

(1) Paper III in this series, C. H. DePuy and D. H. Froemdsdorf, *THIS JOURNAL*, **82**, 634 (1960).

(2) This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of these funds.

(3) W. H. Saunders, Jr., and D. H. Edison, *THIS JOURNAL*, **82**, 138 (1960).

(4) C. H. DePuy and D. H. Froemdsdorf, *ibid.*, **79**, 3710 (1957).

(5) W. H. Saunders, Jr., and R. A. Williams, *ibid.*, **79**, 3712 (1957).

(6) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapt. VII.

(7) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(8) D. J. Cram in "Steric Effects in Organic Chemistry," edited by M. S. Newman, J. Wiley and Sons, Inc., New York, N. Y., 1956, Chapt. 6.

(9) D. J. Cram, F. D. Greene and C. H. DePuy, *THIS JOURNAL*, **73**, 790 (1956).

nylethyl bromides, iodides and tosylates in *t*-butyl alcohol are recorded in Table I. The rates were determined acidimetrically and olefin yields spectrophotometrically. Where possible the rates were measured at two temperatures so that entropies and enthalpies of activation could be calculated. These data, together with some literature values for the eliminations in ethanol, are collected in Table III. The Hammett correlations for the eliminations are reported in Table II. The corresponding sulfonium salts, which had been studied earlier in ethanol solution, could not be investigated in *t*-butyl alcohol because they were not sufficiently soluble.

TABLE I
RATES OF THE ELIMINATION REACTION OF β -PHENYLETHYL DERIVATIVES IN *t*-BUTYL ALCOHOL

Y	Base	T, °C.	Olefin yield, %	$k_{B_2} \times 10^{+4}$, l./mole-sec. ^b
YC ₆ H ₄ CH ₂ CH ₂ I				
H	<i>t</i> -BuOK	30	100	405 ± 10
<i>p</i> -Cl	<i>t</i> -BuOK	30	100	1190 ± 30
<i>p</i> -OCH ₃	<i>t</i> -BuOK	30	100	127 ± 2
<i>m</i> -Br	<i>t</i> -BuOK	30	100	2110 ± 70
H	EtOK ^a	30	100	130 ± 3
<i>p</i> -Cl	EtOK ^a	30	100	466 ± 10
<i>p</i> -OCH ₃	EtOK ^a	30	100	43.1 ± 0.8
<i>m</i> -Br	EtOK ^a	30	100	938 ± 39
H	EtOK ^a	50	100	536 ± 23
<i>p</i> -OCH ₃	EtOK ^a	50	100	206 ± 7
YC ₆ H ₄ CH ₂ CH ₂ Br				
H	<i>t</i> -BuOK	30	100	91.1 ± 2.1
<i>p</i> -Cl	<i>t</i> -BuOK	30	100	274 ± 11
<i>p</i> -OCH ₃	<i>t</i> -BuOK	30	100	24.9 ± 0.7
<i>m</i> -Br	<i>t</i> -BuOK	30	100	575 ± 18
H	<i>t</i> -BuOK	50	100	369 ± 8
<i>p</i> -OCH ₃	<i>t</i> -BuOK	50	100	112 ± 4
H	EtOK ^a	30	100	26.2 ± 0.6
<i>p</i> -Cl	EtOK ^a	30	100	98.6 ± 2.0
<i>p</i> -OCH ₃	EtOK ^a	30	100	7.93 ± 0.17
<i>m</i> -Br	EtOK ^a	30	100	244 ± 6
H	EtOK ^a	50	100	115 ± 6
<i>p</i> -OCH ₃	EtOK ^a	50	100	396 ± 14
YC ₆ H ₄ CH ₂ CH ₂ OTs				
H	<i>t</i> -BuOK	30	100	20.3 ± 0.5
<i>p</i> -Cl	<i>t</i> -BuOK	30	100	121 ± 3
<i>p</i> -OCH ₃	<i>t</i> -BuOK	30	96	3.75 ± 0.19
<i>m</i> -Br	<i>t</i> -BuOK	30	100	686 ± 14
H	<i>t</i> -BuOK	50	100	110 ± 4
<i>p</i> -OCH ₃	<i>t</i> -BuOK	50	95	22.1 ± 0.7
H	EtOK ^a	30	75	4.58 ± 0.26
<i>p</i> -Cl	EtOK ^a	30	87	18.7 ± 6
<i>p</i> -OCH ₃	EtOK ^a	30	40	0.96 ± 0.01
H	EtOK ^a	50	75	22.2 ± 0.7
<i>p</i> -OCH ₃	EtOK ^a	50	42	5.95 ± 0.15

^a Five volume per cent. ethanol in *t*-butyl alcohol; see Discussion. ^b Each point is the average of two or more runs with average deviations.

The results of this study, especially when taken in conjunction with the deuterium isotope studies of Saunders and Edison,³ provide striking confirmation of the suggestion that a spectrum of transition states is available to E₂ eliminations. The salient

TABLE II
HAMMETT CORRELATIONS OF RATES OF ELIMINATION OF β -PHENYLETHYL COMPOUNDS AT 30.0°

Cpd.	Solvent	Base	ρ ^a	r ^b	$-\log k_0$ ^c
OTs	EtOH	EtO ⁻	2.27 ± 0.08 ^d	0.999	4.343
OTs	<i>t</i> -BuOH	<i>t</i> -BuO ⁻	3.39 ± .29	.995	2.596
OTs	<i>t</i> -BuOH	EtO ⁻	2.60 ± .06	.999	3.398
Br	EtOH	EtO ⁻	2.14 ± .15 ^e	.989	3.260
Br	<i>t</i> -BuOH	<i>t</i> -BuO ⁻	2.08 ± .02	.999	2.043
Br	<i>t</i> -BuOH	EtO ⁻	2.28 ± .12	.997	2.525
I	EtOH	EtO ⁻	2.07 ± .09 ^e	.996	2.497
I	<i>t</i> -BuOH	<i>t</i> -BuO ⁻	1.88 ± .06	.999	1.388
I	<i>t</i> -BuOH	EtO ⁻	2.07 ± .09	.999	1.834
+					
S(CH ₃) ₂	EtOH	EtO ⁻	2.75 ± .21	.989	2.330

^a Calculated by method of least squares. ^b Correlation coefficient. ^c Calculated value of the intercept; for methods of calculation see ref. 7. ^d From the data of ref. 4 and the newly determined values of olefin yield, 38% for unsubstituted and 13% for *p*-methoxy. ^e Ref. 4.

TABLE III
ENTROPIES AND ENTHALPIES OF ACTIVATION FOR ELIMINATIONS FROM YC₆H₄CH₂CH₂X

X	Y	Solvent	Base	T, °C. ^a	H* ^b , kcal.-mole ⁻¹	S* ^c , cal.-mole ⁻¹ , °C. ⁻¹
OTs	H	EtOH	EtO ⁻	42	20.4 ^d	-11.2
OTs	H	<i>t</i> -BuOH	<i>t</i> -BuO ⁻	40	14.7	-25.2
OTs	H	<i>t</i> -BuOH	EtO ⁻	40	15.8	-18.7
OTs	<i>p</i> -OCH ₃	EtOH	EtO ⁻	42	20.4 ^d	-13.9
OTs	<i>p</i> -OCH ₃	<i>t</i> -BuOH	<i>t</i> -BuO ⁻	40	16.6	-19.3
OTs	<i>p</i> -OCH ₃	<i>t</i> -BuOH	EtO ⁻	40	17.1	-25.3
Br	H	EtOH	EtO ⁻	45	20.4 ^e	-6.8 ^e
Br	H	<i>t</i> -BuOH	<i>t</i> -BuO ⁻	40	13.0	-25.0
Br	H	<i>t</i> -BuOH	EtO ⁻	40	13.8	-25.0
Br	<i>p</i> -OCH ₃	EtOH	EtO ⁻	50	20.8 ^e	-7.3 ^e
Br	<i>p</i> -OCH ₃	<i>t</i> -BuOH	<i>t</i> -BuO ⁻	40	14.0	-24.3
Br	<i>p</i> -OCH ₃	<i>t</i> -BuOH	EtO ⁻	40	15.0	-23.2
I	H	<i>t</i> -BuOH	EtO ⁻	40	13.2	-23.8

^a Midpoint of the temperature range of the data. ^b Calculated from the slope (method of least squares) of a log *k* vs. 1/*T* plot and the equation $H^* = E_a - RT$. ^c Calculated from the intercept of a log *k* vs. 1/*T* plot. ^d From the rate data of the Ph. D. Thesis of D. H. Froemsdorf, Iowa State University, 1959, and the olefin composition 38% at 30° and 55°. ^e From ref. 4.

facts of the argument can be seen in Table II. With ethoxide ion in ethanol the bromides and iodides show nearly identical Hammett ρ -values, indicating that the amount of negative charge generated on the benzyl carbon in the transition state is about the same in both cases. When the stronger base *t*-butoxide ion in *t*-butyl alcohol is used as the reagent, the reaction rate is increased, but the amount of charge on the benzyl carbon, as measured by ρ , remains the same.

These results are to be contrasted with those for the elimination of the tosylates. In ethanol the ρ for the reaction is slightly greater for the tosylates than it is for the halides. When a stronger base is used for the eliminations, the ρ -value greatly increases, indicating that carbon-hydrogen bond-breaking has progressed further and that the benzyl carbon has a greater negative charge. With the tosylates then, ρ increases drastically with an increase in base strength, while with the halides

it does not increase. The most logical explanation for the difference is that the elimination of the halides is a more highly concerted process, with carbon-halogen and carbon-hydrogen bond breaking being very closely tied. As a consequence, the additional negative charge introduced into the molecule by the stronger base resides, in the case of the halides, not on the benzyl carbon but rather on the leaving group. For reasons which are not yet clear (*vide infra*), the tosylate eliminations are less highly synchronous and the added charge remains more highly concentrated on the benzyl carbon. That the results are due to the strength of the base and not merely to the nature of the solvent is shown by the fact that ρ drops nearly to its former value when ethoxide ion in *t*-butyl alcohol is used for the eliminations.

This argument, although persuasive in its own right, is strengthened by the kinetic isotope effects recently reported by Saunders and Edison.³ With ethoxide as the base they found that the tosylates showed a smaller kinetic deuterium isotope effect ($k_H/k_D = 5.66$) than the bromides ($k_H/k_D = 7.11$). Both these values rose with *t*-butoxide, to 8.01 and 7.89, respectively. With halides and tosylates then, carbon-hydrogen bond breaking increases with the stronger base, yet only with the latter did the charge on the benzyl carbon increase (as measured by ρ). Considering the results with ethoxide in ethanol alone, the tosylates exhibited a larger ρ -value and at the same time a smaller amount of carbon-hydrogen bond-breaking. This result is most consistent with the theory that the tosylate group is removing less of the negative charge from the system than is the bromide, and consequently that carbon-oxygen bond breaking has not progressed as far in the transition state as in the case of the bromide.

It therefore appears reasonable to assume that the transition state for the E_2 reaction, at least in this system, has a great deal of flexibility, varying with the nature of the leaving group and the base. With the halides the use of a stronger base leads not only to a greater amount of carbon-hydrogen bond breaking, but also to a transition state with more double-bond character. With tosylates the situation is rather different. Carbon-oxygen bond-breaking is relatively less important and does not increase as fast with the strength of the base. These conclusions are, of course, derived from the β -phenylethyl system with its relatively activated hydrogens. But this difference might be expected to appear to a certain extent in many different systems.

The entropies and enthalpies of activation for the eliminations are recorded in Table III. The rates of reaction increase in the less polar solvent *t*-butyl alcohol (Table IV), in agreement with the predictions of Ingold¹⁰ that reactions which involve a dispersal of charge in the transition state will be somewhat faster in solvents of lesser solvating power. The moderate increase in rate for the elimination is due, as is often the case,¹¹ to the opposition of large effects in entropy and enthalpy,

the reaction of the bromide with *t*-butoxide being favorable energetically by a factor of 10^4 and being unfavorable in terms of entropy by a factor of 10^5 . The entropy and enthalpy values for the reactions with ethoxide in *t*-butyl alcohol show that these values are primarily a function of the solvent and not of the base. In connection with the use of the mixed solvents, it might be pointed out that there are no data on the relative acidity of ethanol and *t*-butyl alcohol in *t*-butyl alcohol solution. It might be argued that in a 5% ethanol-*t*-butyl alcohol mixture the dominant reactive species is not ethoxide but rather *t*-butoxide. In our view the fact that the rates in this solution are slower by a factor of five than those in pure *t*-butyl alcohol and, more importantly, that the ether-olefin product ratios with the tosylates more nearly correspond to the ratios found with ethoxide in ethanol than to the ratios found with pure *t*-butoxide, makes the nature of the reacting base reasonably certain.

TABLE IV
RELATIVE REACTIVITY OF BROMIDES, IODIDES AND TOSYLATES IN SOME DISPLACEMENT AND ELIMINATION REACTIONS
 $C_6H_5CH_2CH_2X + Y^-$

X	Y	Solvent	Rel. rate E_2	Rel. rate SN2
OTs	EtO ⁻	EtOH	1	2
Br	EtO ⁻	EtOH	11	0.2
I	EtO ⁻	EtOH	68	0.5
OTs	<i>t</i> -BuO ⁻	<i>t</i> -BuOH	52(1)	
Br	<i>t</i> -BuO ⁻	<i>t</i> -BuOH	233(4.5)	
I	<i>t</i> -BuO ⁻	<i>t</i> -BuOH	1030(20)	
OTs	EtO ⁻	<i>t</i> -BuOH	11(1)	
Br	EtO ⁻	<i>t</i> -BuOH	61(5.6)	
I	EtO ⁻	<i>t</i> -BuOH	300(27)	

Table IV summarizes the relative rates of elimination in the systems we studied. We also used gas chromatography to determine the small amount of substitution occurring with the bromides (3%) and iodides (1%) in ethanol. From these data and the rate constants of reference 4 we calculated the relative rates of reaction of these compounds in the SN2 reaction. It is obvious that in the displacement reaction the tosylates are the most reactive of the three leaving groups studied and that they are the least reactive in the elimination reaction. In solvolysis reactions tosylates are very much more reactive than bromides.¹² It appears pertinent to ask why tosylate is a better leaving group than bromide under solvolysis and displacement conditions and a poorer one under the conditions of this elimination reaction. A plausible explanation of this behavior is that the tosylate anion is very stable because of the strong inductive effect of the adjacent sulfur atom and also because of a large amount of resonance stabilization. The contribution of this resonance effect to the stability of the anion should be strongly dependent on the amount of carbon-oxygen bond breaking, being relatively unimportant when there is little bond breaking. For solvolysis reactions, where the carbon-oxygen bond is almost completely broken in the transition state, the tosylate is a better leav-

(10) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 345.

(11) J. E. Löffler, *J. Org. Chem.*, **20**, 1202 (1955).

(12) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

ing group than the bromide. For the elimination reaction, where carbon-oxygen bond breaking is less complete, only the inductive component of anion stabilization may be operative and the tosylate group should be a poorer leaving group than the bromide. If this idea is correct it suggests that it may be possible, in carefully controlled cases, to use bromide-tosylate rate ratios as a measure of bond breaking in the transition state.¹³ It may also be possible to account for the rate differences in terms of differences in solvation of the leaving groups.

From the total rates of reaction with ethoxide ion and the olefin yields it is possible to calculate rates for the SN₂ reaction of the tosylates. These data are recorded in a Hammett plot in Fig. 1. Plotted on the same figure are the data of Baddeley and Bennett¹⁴ for the reaction of substituted β -phenylethyl chlorides with sodium iodide in acetone. The correlation is rather poor and leads to slopes of about +0.6. A better correlation and a higher slope ($\sim +1$) is obtained if the *p*-methoxy points are left out of each series. The slope is a reasonable one for a transition state which, while insulated from the benzene ring, contains a full negative charge.

Experimental

Purification of *t*-Butyl Alcohol.—Unless the *t*-butyl alcohol was carefully dried, the kinetic data, while consistently using the same batch of solvent, varied from batch to batch. Rates determined with *t*-butyl alcohol which was distilled only once from sodium were 10–20% slower than rates from runs using more carefully dried solvent. Two distillations from sodium were sufficient, no further increase in rate being obtained on further drying.

Kinetics.—The data were obtained as previously described,⁴ except that the olefin yields were determined spectrophotometrically.⁵

Determination of Percentage Ether.—The amount of β -phenylethyl ethyl ether arising from the reaction of β -phenylethyl bromide and iodide with ethoxide in ethanol was determined by gas chromatography. The instrument was

(13) It has been pointed out recently that the difference in polarizability of tosylate and halide may be important in determining the relative rates of some displacement reactions; E. L. Eliel and R. G. Haber, *THIS JOURNAL*, **81**, 1249 (1959).

(14) G. Baddeley and G. M. Bennett, *J. Chem. Soc.*, 1819 (1935).

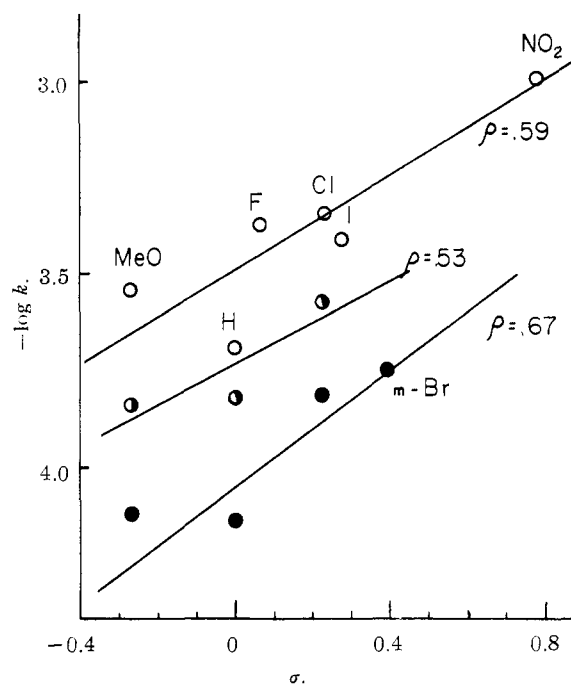


Fig. 1.—Hammett plots for SN₂ displacement of β -phenylethyl compounds: O, chlorides with iodide ion in acetone¹⁴; \bullet , tosylates with ethoxide ion in *t*-butyl alcohol; \circ , tosylates with ethoxide ion in ethanol.

calibrated by analysis of a mixture from the reaction of β -phenylethyl tosylate with ethoxide ion, for which the ether-olefin ratio could accurately be determined spectrophotometrically.

A solution in ethanol containing 0.2 *M* β -phenylethyl tosylate, bromide or iodide and 0.4 *M* sodium ethoxide was allowed to react completely at 30.0°. The resultant solution was diluted with water and extracted with pentane. The extracts were dried and concentrated by careful fractionation of the pentane. The concentrate, still containing large amounts of pentane, was analyzed on a column of 1/3 silicone oil and 2/3 Apiezon L on firebrick at 185°. From the bromide 3% ether was formed and from the iodide, 1%. These yields are probably correct to within 25% or less of their values.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY]

Electronic Effects in Elimination Reactions. V. The E₂ Reaction of β -Phenylethyl Fluorides and Chlorides^{1,2}

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The rates of the bimolecular elimination reaction of a series of *m*- and *p*-substituted β -phenylethyl fluorides and chlorides in ethanolic sodium ethoxide have been determined at 60 and 80°. A Hammett treatment of the data shows that ρ for the reaction of the chlorides is +2.6 and for the fluorides is +3.1 at 30°. Entropies and enthalpies of activation for the reactions have also been calculated. In both cases elimination is much faster than substitution, but the small amount of the latter occurring could be detected by gas chromatography.

Recent studies of the mechanisms of the E₂ reaction of β -phenylalkyl derivatives have em-

(1) Paper IV in this series, C. H. DePuy and C. A. Bishop, *THIS JOURNAL*, **82**, 2532 (1960).

(2) This research was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of these funds.

phasized the dual character of the elimination: the carbanionic character of the β -carbon in the transition state^{3,4} and the close coupling of carbon-

(3) C. H. DePuy and D. H. Froemsdorf, *THIS JOURNAL*, **79**, 3710 (1957).

(4) W. H. Saunders, Jr., and R. A. Williams, *ibid.*, **79**, 3712 (1957).