

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).

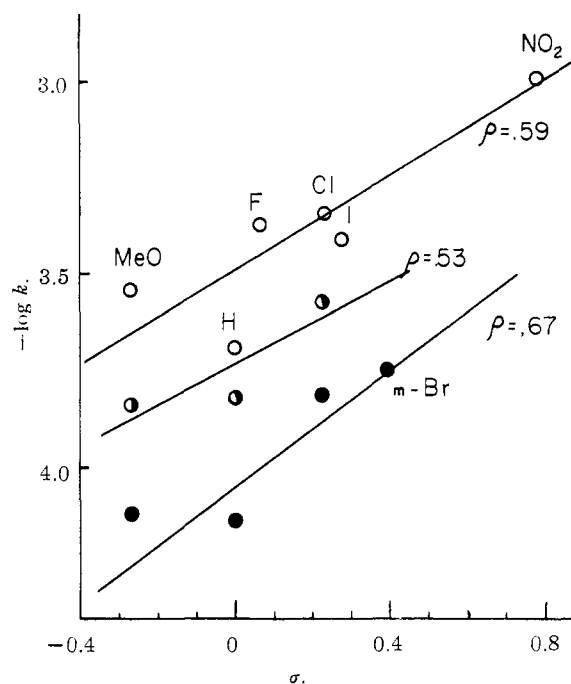


Fig. 1.—Hammett plots for SN₂ displacement of β -phenylethyl compounds: O, chlorides with iodide ion in acetone¹⁴; \bullet , tosylates with ethoxide ion in *t*-butyl alcohol; \circ , tosylates with ethoxide ion in ethanol.

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}

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

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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).

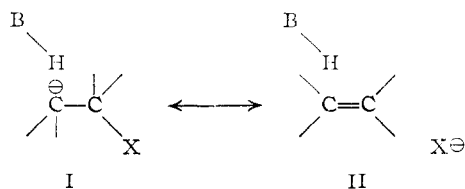
(2) This research was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of these funds.

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).

hydrogen and carbon-halogen bond breaking.^{1,5,6} It seems clear that the leaving group may influence the reaction electronically in at least two ways; *viz.*, inductively by acidifying the β -hydrogen and consequently making its removal easier (*i.e.*, I), and by synchronous bond breaking so that the negative charge is removed from the molecule



and resides, to a greater or lesser degree, on the leaving group (*i.e.*, II). Evidence now favors the view^{1,6} that in eliminations of tosylates and sulfonium salts, stabilization of the second type is less important than in eliminations of bromides and iodides.

Elimination studies with other leaving groups are scarce, and the few available data are contradictory. Cristol and co-workers⁷ studied substituent effects for the elimination of 2,2-diphenyl-1,1-dichloro- and 1,1,1-trichloroethane and found the reaction rate to be very sensitive to the presence of acidifying groups on the benzene ring, ρ^8 for the reaction being +2.456 and +2.729, respectively. Simonetta and Favini,⁹ on the other hand, reported that ρ for the reaction of β -phenylethyl chlorides with hydroxide ion in alcohol-water solution was only 0.0165.¹⁰ In this paper we report an examination of the E_2 elimination of a series of *m*- and *p*-substituted α -phenylethyl chlorides under conditions suitable for comparison with the data previously reported for bromides, iodides, tosylates and sulfonium salts.³ Similar elimination data for substituted β -phenylethyl fluorides is also presented and comprises the first kinetic data on the E_2 reaction involving fluorine as a leaving group. The studies have been conducted at two temperatures and entropies and enthalpies of activation of the reactions have been calculated. The small amount of substitution occurring simultaneously has been determined for the parent (unsubstituted) compound.

The kinetic data for the elimination reactions of the fluorides and chlorides are reported in Table I. The substrates were prepared in each case by the reaction of the corresponding tosylate with sodium halide in diethylene glycol.¹¹ The reactions proceeded smoothly at 100°. In both cases yields of the order of 50% were obtained.

(5) D. J. Cram, F. D. Greene and C. H. DePuy, *THIS JOURNAL*, **78**, 790 (1956).

(6) W. H. Saunders, Jr., and D. H. Edison, *ibid.*, **82**, 138 (1960).

(7) S. J. Cristol, N. L. Hause, A. J. Quant, H. W. Miller, K. R. Eilar and J. S. Meek, *ibid.*, **72**, 3333 (1952).

(8) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chap. VII; (b) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(9) M. Simonetta and G. Favini, *J. Chem. Soc.*, 1840 (1954).

(10) Recalculation of ρ from the data of ref. 9 shows that it is actually +1.65.

(11) (a) E. D. Bergmann and I. Shahak, *Chemistry & Industry*, 157 (1958); (b) F. I. M. Pattison and J. E. Millington, *Can. J. Chem.*, **34**, 757 (1956).

TABLE I
RATES OF THE ELIMINATION REACTION OF β -PHENYLETHYL CHLORIDES AND FLUORIDES WITH ETHANOL

Y-C ₆ H ₄ -CH ₂ CH ₂ X			
Y	X	T, °C.	k _{E2} × 10 ⁵ , l./mole-sec. ^a
H	Cl	60.0	24.1 ± 1.5
<i>p</i> -Cl	Cl	60.0	119 ± 2
<i>m</i> -Br	Cl	60.0	240 ± 9
H	Cl	80.0	185 ± 6
<i>p</i> -Cl	Cl	80.0	855 ± 8
<i>m</i> -Br	Cl	80.0	1810 ± 40
H	Cl	30.0	0.68 ^b
H	F	60.0	0.45 ± 0.017
<i>p</i> -Cl	F	60.0	2.36 ± .06
<i>m</i> -Br	F	60.0	7.28 ± .15
H	F	80.0	4.22 ± .17
<i>p</i> -Cl	F	80.0	22.6 ± .7
<i>m</i> -Br	F	80.0	67.8 ± 2
H	F	30.0	0.01 ^c

^a The olefin yield, in each case, was 100 ± 3%. Each point is the average of two or more runs with average deviations. The rates were corrected for solvent expansion.

^b Calculated from the data at higher temperatures. In one run at 30° a k of 6.67 × 10⁻⁶ was found for the unsubstituted chloride. ^c Calculated from the data at higher temperatures.

As can be seen from Table II, the ρ -value for the eliminations increases monotonically as one goes from I to Br to Cl to F. In the last case, the ρ (+3.12) is the highest yet found for an elimination in ethanol. It seems then, that the inductive effect of the fluorine and chlorine plays a dominant role in the elimination by acidifying the β -hydrogens. The fact that the rate of elimination varies inversely as the value of ρ among the halogens shows again the importance of carbon-halogen bond breaking in determining the over-all rate of the reaction.

TABLE II
HAMMETT CORRELATIONS OF THE RATES OF ELIMINATION OF β -PHENYLETHYL COMPOUNDS WITH ETHOXIDE IN ETHANOL

Cmpd.	T, °C.	ρ^a	τ^b	$-\log k_0^c$
Cl	60	2.58 ± 0.33	0.991	3.586
Cl	80	2.56 ± .25	.994	2.708
Cl	30	(2.61) ^d		
F	60	3.10 ± .07	.999	5.360
F	80	3.09 ± .08	.999	4.367
F	30	(3.12) ^d		
Br ^e	30	2.14 ± .15	.989	3.260
I ^e	30	2.07 ± .09	.999	2.497
⁺ S(CH ₃) ₂ ^e	30	2.75 ± .21	.989	2.330

^a Calculated by the method of least squares. ^b Correlation coefficient. ^c Calculated value of the intercept; for methods of calculation, see ref. 7b. ^d Calculated from the values at higher temperatures assuming a linear relationship between T and ρ . ^e Ref. 3.

The slower elimination rate of the fluorides and chlorides as compared to the bromides and iodides seems to be due entirely to a difference in enthalpy of activation, the entropies being, if anything, slightly more favorable. The relative rates of elimination are F:Cl:Br:I = 1:70:4300:28,000.

By gas chromatographic analysis of the products of reaction we found it possible to measure the small amount of substitution occurring simulta-

TABLE III
ENTROPIES AND ENTHALPIES OF ACTIVATION FOR ELIMINATIONS FROM $Y-C_6H_4-CH_2CH_2-X$

Y	X	T, °C. ^a	H^\ddagger , kcal./mole ^b	S^\ddagger , cal./mole, °C. ^c
H	Cl	70	23.2	-5.6
<i>p</i> -Cl	Cl	70	22.4	-4.8
<i>m</i> -Br	Cl	70	23.0	-1.1
H	F	70	25.3	-5.4
<i>p</i> -Cl	F	70	25.8	-2.5
<i>m</i> -Br	F	70	25.5	-1.2
H	Br	45	20.4 ^d	-6.8 ^d

^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 $H^\ddagger = E_a - RT$. ^c Calculated from the intercept of a $\log k$ vs. $1/T$ plot. ^d Ref. 4.

neously with elimination. The approximate yields of β -phenylethyl ether were for the fluoride 1%, and for the chloride, 3%. These values compare closely to the amounts of substitution occurring with the bromides and iodides and show that, despite the acidity of the benzyl hydrogen being removed, the E_2 and SN_2 reactions change in an analogous way as the nature of the halogen-leaving group changes.

Acknowledgment.—We wish to thank Miss Carol Jean Schultz for technical assistance.

Experimental

Preparation of β -Arylethyl Fluorides.—The arylethyl tosylates were heated with an excess of potassium fluoride in diethylene glycol.¹¹ As a typical example, β -phenylethyl tosylate (5.0 g., 0.04 mole) and potassium fluoride dihydrate (11.2 g., 0.12 mole) were dissolved in 25 ml. of diethylene glycol and stirred at 100° for 20 hours. At the end of this time the initially heterogeneous system had become homo-

geneous. The solution was cooled and poured into 100 ml. of water and extracted with pentane. After washing and drying the extracts, the pentane was carefully removed and the product distilled.

β -Phenylethyl fluoride: 51% yield, b.p. 55–56° (12 mm.). *Anal.* Calcd. for C_8H_9F : C, 77.4; H, 7.30. Found: C, 77.5; H, 7.29.

β -(*p*-Chlorophenyl)-ethyl fluoride: 43% yield, b.p. 79–80° (9 mm.). *Anal.* Calcd. for C_8H_9ClF : C, 60.58; H, 5.08; Cl, 22.36. Found: C, 60.88; H, 5.13; Cl, 22.08.

β -(*m*-Bromophenyl)-ethyl fluoride: 45% yield, b.p. 80–81° (4 mm.). An insufficient amount of this compound was available for purification of an analytical sample. Gas phase chromatographic analysis showed it to be greater than 99% pure and the rate constants were calculated from experimental infinity points.

Preparation of β -Arylethyl Chlorides.—Arylethyl tosylates were heated with a 4:1 molar excess of lithium chloride in diethylene glycol in a procedure analogous to that for the preparation of the arylethyl fluorides.

β -Phenylethyl chloride: 69% yield, b.p. 81–83° (14 mm.). (lit.⁹ b.p. 83–84° (14 mm.)).

β -(*p*-Chlorophenyl)-ethyl chloride: 41% yield, b.p. 82–83° (3 mm.). (lit.¹² b.p. 133° (35 mm.)).

β -(*m*-Bromophenyl)-ethyl chloride: 56% yield, b.p. 80–81° (1 mm.). An insufficient amount of this compound was available for purification of an analytical sample. Gas phase chromatographic analysis showed it to be greater than 99% pure and the rate constants were determined from experimental infinity points.

Kinetic Measurements.—Reactions were carried out in ampules of 10-ml. capacity each of which contained a 5-ml. sample. The samples were pipetted at 30° and appropriate corrections for volume expansion at a higher temperature were made in the calculations of rates.

The reactions were followed acidimetrically and olefin determinations were made spectrophotometrically.

Olefin determinations were made on the unsubstituted chloride and fluoride by gas phase chromatography technique.

(12) G. Baddeley and G. M. Bennett, *J. Chem. Soc.*, 1820 (1935).

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[CONTRIBUTION FROM ROHM & HAAS CO.]

A New Preparation of 1,3,5-Hexatriene and the Separation of its Geometrical Isomers

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RECEIVED AUGUST 31, 1959

Mixtures of *cis*- and *trans*-1,3,5-hexatriene were prepared from bromohexadienes by quaternization followed by Hofmann elimination. The separation of isomers has been carried out, and physical, spectral and chemical properties of the *cis* isomer determined for the first time. The *cis* isomer was shown to be obtained only in trace amounts by previously reported pyrolytic methods.

Recent descriptions of the preparation of 1,3,5-hexatriene^{1,2} have presented more consistent and complete data on its properties than have many other past reports.³ These recent preparations have both been characterized as the *trans* isomer.^{2,4} In only one case^{3c} has a definite claim been made of the preparation of the *cis* isomer. In our work, a

new method of preparation of 1,3,5-hexatriene was developed, and from the hydrocarbon we have separated what we believe to be the pure *cis* and *trans* isomers. Our data do not agree with that given in this previous reference to the *cis* isomer.

We have prepared 1,3,5-hexatriene (I) by a Hofmann elimination under much milder conditions than those described in previous publications, from 1,5-hexadien-3-ol (II), according to the reaction scheme illustrated by the formula diagram. The lower temperature used in this synthesis has allowed the preparation of I containing substantial proportions of both isomers and completely free of cyclohexadiene. This is in contrast to most pyrolytic methods.²

The synthesis was most easily carried out without purification of intermediates to give I in 60%

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(4) E. Lippincott, C. White and J. Sibilla, *THIS JOURNAL*, **80**, 2926 (1958).