[Contribution from the Department of Chemistry, Iowa State College]

Electronic Effects in Elimination Reactions. II. The E_2 Reaction[1a,b]

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The base-promoted elimination reaction of substituted β-phenylethyl halides, tosylates and sulfonium salts has been studied as a function of substituents. Good fits to a Hammett σ–ρ plot were obtained, indicating that the acidity of the hydrogen being removed is controlling the direction of elimination. In contrast to their reactivity in solvolysis and displacement reactions, tosylates are eliminated very slowly as compared to bromides and iodides.

In connection with a general study of electronic effects in elimination reactions,[1b] we were led to an investigation of the electronic effects in the E_2 reaction, both because of the interest in the reaction for its own sake[2] and because such a study would serve as a reference for our investigation in the similar 1,3-diphenylpropyl system. Surprisingly, no comprehensive investigation of substituent effects on E_2 eliminations has been reported[3] except for some polyhalo compounds[4] and for a few β-phenylethyl chlorides.[5] Quantitative data on E_2 tosylate eliminations are likewise unavailable.[6]

Our data for the elimination of β-phenylethyldimethylsulfonium iodide, β-phenylethyl bromide, iodide and tosylate are summarized in Tables I and II. For the sulfonium salts $\rho = 2.75 \pm 0.21$, the highest value of ρ for the series. For the bromides $\rho = 2.14 \pm 0.15$ and for the iodides $\rho = 2.07 \pm 0.09$. Omitting the point for the *p*-methoxy group, $\rho = 2.50 \pm 0.06$ for the tosylates. A high positive value for ρ implies that in the transition state of the reaction a large amount of negative charge has developed, and those groups which make a negative charge more stable speed up the reaction.[7]

It has been suggested that the Saytzeff rule is a consequence of a transition state in which the stability of the incipient double bond is the dominant characteristic.[2a,8] Our results indicate that when the hydrogen being removed is on a carbon adjacent to a benzene ring, the stability of the product being formed is not of importance,[9] for if it were the *p*-methoxystyrene should be formed most rapidly.[1b,10] The fact that the sulfonium salts, bromides and iodides, and to a major extent the tosylates,[9] all show a good correspondence of rate with a measure of hydrogen acidity is to be contrasted with our results with acetate pyrolysis reactions in which a good correlation with product stability was observed[1b] in an analogous system. In these two cases we have demonstrated the extremes of transition state structural variation, from one in which double bond development is too small to be significant (E_2) to one in which the stability of the double bond being formed determines the rate of elimination.

Table I

Rates of the Elimination Reaction of $XC_6H_4CH_2CH_2Y$ at 30.10°

X	Y	k	Olefin, %	k_{E2}
H	Br	4.10×10^{-4}	100	4.10×10^{-4}
p-Cl	Br	1.88×10^{-3}	100	1.88×10^{-3}
p-OCH_3	Br	1.73×10^{-4}	100	1.73×10^{-4}
m-Br	Br	3.71×10^{-3}	100	3.71×10^{-3}
H	I	2.66×10^{-3}	100	2.66×10^{-3}
p-Cl	I	1.05×10^{-2}	100	1.05×10^{-2}
p-OCH_3	I	9.56×10^{-4}	100	9.56×10^{-4}
m-Br	I	2.03×10^{-2}	100	2.03×10^{-2}
H	OTos	1.18×10^{-4}	33	3.92×10^{-5}
p-Cl	OTos	2.93×10^{-4}	47	1.38×10^{-4}
p-OCH_3	OTos	$8.61 \times 10_{5}^{-}$	20	1.69×10^{-5}
m-Br	OTos	5.53×10^{-4}	67	3.69×10^{-4}
H	$\overset{+}{S}(CH_3)_2I^-$	3.79×10^{-3}	100	3.79×10^{-3}
p-Cl	$\overset{+}{S}(CH_3)_2I^-$	2.18×10^{-2}	100	2.18×10^{-2}
p-CH_3	$\underset{+}{S}(CH_3)_2I^-$	9.13×10^{-4}	100	9.13×10^{-4}

Table II

	ρ (method of least squares)	$\log k_0$ (calcd.) Intercept
Tosylates (omitting *p*-methoxy)	2.50 ± 0.06	-4.427
Tosylates (including *p*-methoxy)	$2.04 \pm .47$	-4.280
Bromides	$2.14 \pm .15$	-3.260
Iodides	$2.07 \pm .09$	-2.497
Sulfonium salts	$2.75 \pm .21$	-2.330

The fact that the ρ-value for the sulfonium salts is larger than that for the bromides and iodides implies that the transition state for Hofmann eliminations has significantly more carbanionic character than that for the elimination of iodides or bromides. Whether this difference would be enough to account for some of the differences in direction of halide and 'onium salt eliminations in strictly aliphatic systems[2] cannot yet be said with certainty.

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[1] (a) Supported by a Grant-in-Aid from the Monsanto Chemical Co. Presented in part at the 130th Annual Meeting of the American Chemical Society, Atlantic City, N. J., September 16–21, 1956. (b) Paper I in this series, C. H. DePuy and R. E. Leary, This Journal, **79**, 3705 (1957).

[2] (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, p. 420; (b) W. H. Saunders and R. A. Williams, This Journal, **79**, 3712 (1957).

[3] At the time of our preliminary announcement of some of these results, we were informed by Dr. W. H. Saunders of the results of some excellent work that was being done in his laboratory along similar lines.[2b] The existence of these data, more complete than our own in terms of the temperature range studied but confined to two leaving groups, has influenced the presentation of our data. We shall be content to point out a few conclusions pertinent to our main interests and to refer the reader to the report of Dr. Saunders for much of the background. We are grateful to Dr. Saunders for interesting discussions and for data on the extinction coefficients of some of the olefins.

[4] S. J. Cristol, N. L. Hause, A. J. Quant, H. W. Miller, K. R. Eilar and J. S. Meek, This Journal, **72**, 3333 (1952).

[5] M. Simonetta and G. Favini, *J. Chem. Soc.*, 1840 (1954).

[6] *Cf.* R. P. Linstead, L. N. Owen and R. F. Webb, *ibid.*, 1218 (1953).

[7] See R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 556, for a discussion of the mechanistic interpretation of ρ.

[8] H. C. Brown and I. Moritani, This Journal, **78**, 2203 (1956).

[9] See, however, the discussion of the deviation of the *p*-methoxyl tosylate.

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

Perhaps the most surprising result of this investigation is the very slow rate of elimination of the tosylates. For the unsubstituted cases, $k_I/k_{Tos} = 68$ and $k_{Br}/k_{Tos} = 10$. In the case of direct displacement reactions, sulfonic acid esters appear to be more reactive than either bromides or iodides,[11] although admittedly the data are meager. This slowness in the elimination reaction has a synthetic as well as a theoretical value. From Table I it can be seen that the percentage olefin in the product varies from 20 to 67% for the tosylate eliminations. In all other cases of leaving groups studied, the olefin yield was close to 100%. Hence, while the E_2 reaction is slow, apparently the S_N2 reaction remains fast. For this reason the tosylate can be useful in preparing the corresponding ethers or amines[12] when the iodides and bromides lead only to olefin. The meagerness of available data makes a firm theoretical conclusion hazardous, and we shall discuss in subsequent papers the results of a more detailed study of tosylate elimination. The *p*-methoxy tosylate eliminates significantly faster than would be predicted on the basis of the ρ-value of the reaction. This may imply that, in this relatively unactivated case, some effect of the olefin stability is being felt in the transition state.

Experimental

Preparation of 2-Arylethanols. 2-(*m*-Bromophenyl)-ethanol.—*m*-Bromoacetophenone was prepared by bromination of acetophenone in the presence of excess anhydrous aluminum chloride.[13] This was transformed into *m*-bromophenylacetic acid by heating under reflux for 16 hr. 103 g. of the ketone with 68 g. of morpholine and 25 g. of sulfur. The resulting thiomorpholide was hydrolyzed by boiling with 10% potassium hydroxide for 18 hr. and then acidifying. The precipitated *m*-bromophenylacetic acid weighed 78.7 g. (70.7% yield) and had m.p. 99–100° (lit.[14] m.p. 100°). Lithium aluminum hydride reduction of the ethyl ester gave the alcohol, b.p. 107–110° (1 mm.).

2-(*p*-Chlorophenyl)-ethanol was prepared by refluxing *p*-chlorobenzyl cyanide with 95% ethanol and concentrated sulfuric acid[15] to yield the ethyl ester of *p*-chlorophenylacetic acid. Reduction with lithium aluminum hydride gave the alcohol (75.5% yield), b.p. 98–100° (1 mm.) (lit.[16] b.p. 110° (0.5 mm.)).

2-(*p*-Methoxyphenyl)-ethanol was prepared from *p*-methoxyacetophenone by the same method[17] as the 2-(*m*-bromophenyl)-ethanol, b.p. 110–113° (1 mm.) (lit.[18] 148° (19 mm.)).

2-Phenylethanol was Eastman Kodak Co. White Label.

Preparation of Tosylates.—The tosylates were prepared from the corresponding alcohol by Tipson's procedure.[19]

2-(*m*-Bromophenyl)-ethyl-*p*-toluenesulfonate, m.p. 43–44°. *Anal.* Calcd. 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°. *Anal.* Calcd. 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°. *Anal.* Calcd. 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°. *Anal.* Calcd. C, 65.20; H, 5.84; S, 11.60. Found: C, 65.45; H, 5.77; S, 11.25.

Preparation of 2-Arylethyl Bromide.—The bromides were prepared by addition of the appropriate tosylate to a solution of anhydrous lithium bromide in acetone[20] and careful fractionation of the resultant bromides: 2-(*m*-bromophenyl)-ethyl bromide, b.p. 98–100° (1 mm.); 2-(*p*-chlorophenyl)-ethyl bromide, b.p. 79° (0.5 mm.); 2-(*p*-methoxyphenyl)-ethyl bromide, b.p. 79° (0.5 mm.); 2-phenylethyl bromide was Eastman Kodak Co. White Label which was redistilled, b.p. 65° (2 mm.).

Preparation of 2-Arylethyl Iodides.—The iodides were prepared by addition of the appropriate tosylate to a solution of anhydrous sodium iodide in acetone[20] and fractionation: 2-(*m*-bromophenyl)-ethyl iodide, b.p. 105–110° (1 mm.); 2-(*p*-chlorophenyl)-ethyl iodide, b.p. 115–117° (1 mm.); 2-(*p*-methoxyphenyl)-ethyl iodide, b.p. 117–119° (1 mm.); 2-phenylethyl iodide was Eastman Kodak Co. White Label which was redistilled, b.p. 95° (3 mm.).

Preparation of Sulfonium Salts.—The sulfonium salts were prepared by treating the appropriate iodide with sodium methylmercaptide[8]; this gave the sulfide. The sulfide was then treated with methyl iodide[8] in acetonitrile which gave the dimethylsulfonium iodide: 2-(*p*-chlorophenyl)-ethyldimethylsulfonium iodide, m.p. 127–128°; 2-(*p*-methoxyphenyl)-ethyldimethylsulfonium iodide, m.p. 118–119°; 2-phenylethyldimethylsulfonium iodide, m.p. 124–125°.

Procedure for Kinetics.—The reactions were carried out in 100-ml. volumetric flasks. About 0.06 mole of the desired compound was placed in the volumetric flask and weighed accurately. Then 0.12 *N* sodium ethoxide in absolute ethanol, previously equilibrated thermally with the bath, was added to the calibration mark of the volumetric flask. After adequate agitation, the flask was placed in the bath and allowed to come to thermal equilibrium. Aliquots were then withdrawn periodically with a calibrated automatic pipet.

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 absolute ethanol and 0.24 *N* sodium ethoxide in absolute ethanol added so the total volume was 100 ml.

Olefin Determinations.—The reactions were allowed to go to completion, and 25-ml. aliquots were poured into water and extracted with carbon tetrachloride (3 × 10 ml.), the extract washed with water and the amount of olefin determined by bromination with standard bromide–bromate solution.[21] 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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(12) See D. J. Cram, F. D. Greene and C. H. DePuy, THIS JOURNAL, **78**, 790 (1956), for a synthetic example.

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

(17) U. V. Solmssen and E. Wenis, THIS JOURNAL, **70**, 4200 (1948).

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(20) H. C. Brown and O. H. Wheeler, THIS JOURNAL, **78**, 2199 (1956).

(21) Sidney Siggia, "Quantitative Organic Analysis *via* Functional Groups," 2nd Ed., John Wiley & Sons, Inc., New York, N. Y., 1954, p. 68.