Electronic Effects in Elimination Reactions. VI. Bimolecular Eliminations from 1-Aryl-2-propyl and 2-Aryl-1-propyl Tosylates and Bromides[1]

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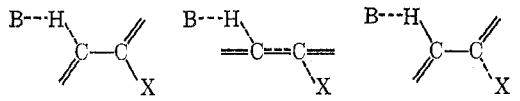
A kinetic study of the bimolecular, base-promoted elimination reactions of the α- and β-methyl-substituted β-phenylethyl tosylates and bromides is reported. The reactions were conducted in potassium *t*-butoxide in *t*-butyl alcohol and sodium ethoxide in ethanol. These compounds are shown to develop less carbanion character in the transition states of their elimination reactions than in those of β-phenylethyl tosylates and bromides. The ρ values and *t*-butoxide:ethoxide rate ratios show that the decrease in carbanion character is greatest for reactions of the α-methyl compounds.

The flexibility of the structure of bimolecular elimination transition states is well documented.[5] Between the extreme anionic, E1cB, and cationic E1 eliminations reside the bimolecular concerted E2 processes whose transition states vary across a mechanism spectrum as shown schematically below. The position of a transition state on this spectrum is determined by the relative amounts of C–H and C–X bond breaking and C–C double-bond character. These in turn are dependent upon the nature of the leaving group, X, the base, B, the substituents on the molecule, the base strength, and the solvent medium.[5c]



E1cB-like central E2 E1-like

Extensive mechanistic studies of E2 reactions have been conducted on β-phenylethyl compounds using as leaving groups halides, *p*-toluenesulfonate (tosylate), dimethyl sulfide, and trimethylamine.[6,7] The overall effect of a 2-aryl substituent is to shift the mechanism toward one of more carbanion character but with the retention of a single, concerted transition state. The degree of carbanion character, as shown by Hammett σ–ρ correlations, increases as the leaving group becomes more electronegative and as β-hydrogen acidity increases. Kinetic isotope effects for both the proton[8a] and various leaving groups,[8b,c] and rate studies in D_2O[9] have complemented these earlier findings for β-phenylethyl compounds.

There have been fewer investigations of substituted β-phenylethyl compounds. The deuterium kinetic isotope effect for elimination of 1-phenyl-2-methyl-2-chloropropane in methoxide–methanol has been measured,[10] and the low value of k_H/k_D has been postulated to reflect the small amount of C–H bond breaking in the transition state. On the other hand, k_H/k_D determined by Shiner and Smith[11] for 2-phenyl-1-bromopropane in sodium ethoxide–ethanol is larger than the theoretical maximum value,[12] and it has been proposed that the high value is a result of quantum-mechanical tunneling.

In this paper we report on rates, solvent effects, and Hammett correlations of a variety of methyl-substituted β-phenylethyl compounds. Our intention was to determine to what extent such substitution would be reflected in detectable and predictable changes in transition state structure, and to give added tests to several different methods for measuring subtle changes in mechanism.

Results and Discussion

In earlier studies[13] we have shown that *trans*-2-phenylcyclopentyl tosylate undergoes a remarkably rapid, bimolecular *syn* elimination reaction in *t*-butoxide–*t*-butyl alcohol solution. Making use of Hammett σ–ρ relationships, we proposed that coplanar *syn* eliminations were in general more E1cB-like than coplanar *anti* eliminations. In drawing these conclusions we used the extensive work on elimination from β-phenylethyl compounds as a standard. The cyclic systems studied, however, were necessarily alkylated β-phenylethyl systems, and few studies of the effect of alkyl substituents on E2 eliminations have been reported. We therefore decided to see how important such substituents are in controlling transition state geometry in acyclic E2 reactions. In Tables I–IV the rates of E2 reaction of β-phenylethyl tosylates and bromides substituted with an α- or a β-methyl group are reported for both *t*-butoxide–*t*-butyl alcohol and ethoxide–ethanol solution. In Table V Hammett correlations and activation parameters are reported, and in

(1) Part V: C. H. DePuy, G. F. Morris, J. S. Smith, and R. J. Smat, *J. Amer. Chem. Soc.*, **87**, 2421 (1965). This work was supported in part by the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is made to the donors of said funds.

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TABLE I

RATE CONSTANTS FOR ELIMINATION FROM 1-ARYL-2-PROPYL TOSYLATES AND BROMIDES, Y-$C_6H_4CH_2CH(CH_3)$-X, IN POTASSIUM *t*-BUTOXIDE–*t*-BUTYL ALCOHOL SOLUTION

X	Y	Temp, °C	$k_{E2} \times 10^4$[a] l. mol^{-1} sec^{-1}	1-Aryl-1-propene[b] yield, %
OTs	H	50.0	9.32 ± 0.10[c]	98
OTs	H	30.0	2.39 ± 0.03	
OTs	*p*-Cl	50.0	21.8 ± 0.2	
OTs	*m*-Br	50.0	52.0 ± 0.8	97
OTs	*p*-CH_3	50.0	4.56 ± 0.11	98
OTs	*p*-OCH_3	50.0	2.74 ± 0.04	
Br	H	50.0	94.1 ± 1.0	
Br	*p*-Cl	50.0	177. ± 3	
Br	*m*-Br	50.00	274. ± 6	97
Br	*p*-CH_3	50.0	45.5 ± 0.9	100
OTs	β-Phenylethyl	50.00	110[d]	100
Br	β-Phenylethyl	50.00	369[d]	100

[a] Determined spectrophotometrically. [b] Determined by gas chromatography. The 1-aryl-1-propenes were approximately 5% *cis* and 95% *trans*. The remaining product was 3-aryl-1-propene. [c] Average deviation from the mean of two or more runs. [d] Reference 6b.

TABLE II

RATE CONSTANTS FOR ELIMINATION FROM 1-ARYL-2-PROPYL TOSYLATES AND BROMIDES, Y-$C_6H_4CH_2CH(CH_3)$-X, IN SODIUM ETHOXIDE–ETHANOL SOLUTION

X	Y	Temp, °C	$k_{E2} \times 10^4$[a] l. mol^{-1} sec^{-1}	1-Aryl-1-propene yield, %[b]
OTs	H	50.0	3.42 ± 0.09[c]	81
OTs	H	30.0	0.42 ± 0.02	
OTs	*p*-Cl	50.0	9.85 ± 0.26	
OTs	*p*-Cl	30.0	1.08 ± 0.04	
OTs	*m*-Br	50.0	16.4 ± 0.4	93
OTs	*p*-CH_3	50.0	2.87 ± 0.06	80
OTs	*p*-OCH_3	50.0	2.32 ± 0.10	
OTs	*p*-OCH_3	30.0	0.28 ± 0.01	
Br	H	50.0	19.2 ± 0.4	
Br	H	30.0	2.55 ± 0.04	
Br	*p*-Cl	50.0	85.4 ± 2.0	
Br	*m*-Br	50.0	155. ± 5	97
Br	*m*-Br	30.0	20.9 ± 0.6	
Br	*p*-CH_3	50.0	17.7 ± 0.05	99
OTs	β-Phenylethyl	50.0	5.98[d]	100
Br	β-Phenylethyl	50.0	34.2[d]	100

[a] Determined spectrophotometrically. [b] Determined by gas chromatography. 3-Aryl-1-propene and ethyl ether were the other products. The 1-aryl-1-propenes were approximately 90% *trans* and 10% *cis*. [c] Average deviation from the mean of two or more runs. [d] Reference 6b.

Table VI some of these data are compared with literature values for related compounds.

Looking first at the data for elimination in *t*-butoxide, we see that substitution of β-phenylethyl by either an α- or a β-methyl group decreases the E2 rate for both tosylates and bromides. For the α-CH_3 group the decrease is a factor of 6 and 2, respectively,[14] and for the β-CH_3 group the decrease is a factor of 25 and 5. These rate decreases are most likely due to an inductive

(14) The β-phenylethyl rates must be divided by two to give rates per hydrogen atom, since *trans* olefin is the nearly exclusive product from 1-phenyl-2-propyl tosylate and bromide.

TABLE III

RATE CONSTANTS FOR ELIMINATIONS FROM 2-ARYL-1-PROPYL TOSYLATES AND BROMIDES, Y-$C_6H_4CZ(CH_3)CH_2$-X, IN POTASSIUM *t*-BUTOXIDE–*t*-BUTYL ALCOHOL SOLUTION

X	Y	Z	Temp, °C	$k_{E2} \times 10^4$[a] l. mol^{-1} sec^{-1}	Olefin[b] yield, %
OTs	*p*-H	H	49.8	2.14 ± 0.03[c]	92
OTs	*p*-H	H	29.8	0.34 ± 0.01	93
OTs	*p*-Cl	H	49.8	7.06 ± 0.10	100
OTs	*m*-Br	H	49.8	17.80 ± 0.50	96
OTs	*m*-Br	D	49.8	2.83 ± 0.12	90
OTs	*p*-CH_3	H	49.8	0.93 ± 0.01	90
OTs	*p*-CH_3	D	49.8	0.15 ± 0.01	64
OTs	*p*-OCH_3	H	49.8	0.66 ± 0.01	80
Br	*p*-H	H	49.8	41.10 ± 1.00	100
Br	*p*-H	H	29.8	8.19 ± 0.18	100
Br	*p*-Cl	H	49.8	118.00 ± 3.00	100
Br	*m*-Br	H	49.8	201.00 ± 4.00	98
Br	*m*-Br	D	49.8	26.40 ± 0.10	100
Br	*p*-CH_3	H	49.8	21.10 ± 0.50	100
Br	*p*-CH_3	D	49.8	3.19 ± 0.01	99
Br	*p*-OCH_3	H	49.80	14.70 ± 0.70	96

[a] Determined titrimetrically. [b] Determined spectrophotometrically. [c] Average deviation from the mean of two or more runs.

effect of the methyl, although steric effects may also play a role.[15]

In ethoxide–ethanol the rate effect of a methyl group is more interesting. We have pointed out previously[13] that a shift from *t*-butoxide–*t*-butyl alcohol to ethoxide–ethanol has the effect of moving the transition state in the E1 direction, since the base strength decreases and the ionizing power of the medium increases. Attachment of a β-methyl group still decreases the rate (by a factor of 5 for the tosylate and 1.2 for the bromide) but attachment of an α-methyl group increases the E2 rate slightly in both cases. These results are at least consistent with the view that the greater ionizing power of the ethanol can, in the case of secondary but not primary tosylates and bromides, overcome the inductive effect of a methyl group.

For the tosylates, Hammett correlations and rate ratios in *t*-butoxide–ethoxide, as summarized in Table VI, also show a consistent pattern. In all cases the ρ value is larger in the stronger base, less ionizing solvent. From the ρ values alone one would say that substitution of an alkyl group moves the transition state in the E1 direction, and the *t*-butoxide:ethoxide rate ratios support this conclusion, although the latter effects could also be accounted for by involving steric effects.

The rate ratios and ρ values among the bromides (Table VI) do not show such a perfect correspondence, but the general trend is correct. The usefulness of the solvent rate ratio is perhaps increased if one notes that the tertiary bromide, $C_6H_5CH_2C(CH_3)_2Br$ reacts 7 times *faster* in ethoxide–ethanol than it does in *t*-butoxide–*t*-butyl alcohol.[16] The ρ values for the bromides in Table VI are greater in the less basic, better solvating medium ethoxide–ethanol than in *t*-butoxide–*t*-butyl alcohol. This trend is opposite to that expected on the basis of medium effects[5] and that observed among the tosylates. This anomaly is perhaps best explained by the greater ability of bromide, relative to tosylate, to

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Table IV

Rate Constants for Eliminations from 2-Aryl-1-propyl Tosylates and Bromides, Y-$C_6H_4CZ(CH_3)CH_2$-X, in Sodium Ethoxide–Ethanol Solution

X	Y	Z	Temp, °C	$k_{E2} \times 10^4$[a] l. mol^{-1} sec^{-1}	Olefin[b] yield, %
OTs	*p*-H	H	49.8	0.56 ± 0.02[c]	64
OTs	*p*-H	H	29.8	0.054 ± 0.002	71
OTs	*p*-Cl	H	49.8	1.35 ± 0.01	64
OTs	*m*-Br	H	49.8	2.64 ± 0.02	75
OTs	*m*-Br	D	49.8	0.56 ± 0.04	44
OTs	*p*-CH_3	H	49.8	0.27 ± 0.01	41
OTs	*p*-CH_3	D	49.8	0.066 ± 0.001	15
OTs	*p*-OCH_3	H	49.8	0.28 ± 0.01	28
Br	*p*-H	H	49.8	14.50 ± 0.50	100
Br	*p*-H	H	29.8	1.58 ± 0.02	100
Br	*p*-Cl	H	49.8	58.00 ± 0.10	97
Br	*m*-Br	H	49.8	112.00 ± 1.00	100
Br	*m*-Br	D	49.8	15.90 ± 0.1	95
Br	*p*-CH_3	H	49.8	9.34 ± 0.47	100
Br	*p*-CH_3	H	49.8	1.47 ± 0.01	94
Br	*p*-OCH_3	D	49.8	8.32 ± 0.06	100

[a] Determined titrimetrically. [b] Determined spectrophotometrically. [c] Average deviation from the mean of two or more runs.

Table V

Hammett Correlations and Enthalpies and Entropies of Activation for Eliminations from β-Phenylethyl-X Compounds

Compound	X	Base-solvent	ρ,[a] at 50°	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}
α-CH_3	OTs	*t*-BuOK–*t*-BuOH	1.88 ± 0.03	12.6	−33
α-CH_3	OTs	EtONa–EtOH	1.33 ± 0.07	19.7	−13
α-CH_3	Br	*t*-BuOK–*t*-BuOH	1.37 ± 0.03		
α-CH_3	Br	EtONa–EtOH	1.84 ± 0.11	19.0	−12
β-CH_3	OTs	*t*-BuOK–*t*-BuOH	2.18 ± 0.03	17.2	−22
β-CH_3	OTs	EtONa–EtOH	1.81 ± 0.02[b]	22.0	−9
β-CH_3	Br	*t*-BuOK–*t*-BuOH	1.75 ± 0.02	15.0	−23
β-CH_3	Br	EtONa–EtOH	2.06 ± 0.05[b]	20.9	−6

[a] Calculated by the method of least squares. [b] Omitting *p*-methoxy.

Table VI

Hammett Correlations and *t*-Butoxide–Ethoxide Rate Ratios for Eliminations from 2-Phenyl-Substituted Tosylates at 50°

Compound	ρ (*t*-BuOK–*t*-BuOH)	ρ (EtONa–EtOH)	k_{E2} (*t*-BuOK) / k_{E2} (EtONa)
	Tosylates		
2-Phenylethyl	3.39[a,b]	2.27[a,b]	22.0
2-Phenyl-1-propyl	2.18	1.81	3.9
1-Phenyl-2-propyl	1.88	1.32	2.7
cis-2-Phenylcyclopentyl	1.48[c]	0.99[c]	1.2
	Bromides		
2-Phenylethyl	2.08[a,b]	2.14	11.0
2-Phenyl-1-propyl	1.75	2.06	2.8
1-Phenyl-2-propyl	1.37	1.84	5.0

[a] From ref 6b. [b] Measured at 30°. [c] From ref 13c.

disperse the incipient negative charge at the benzyl carbon in poorly solvating *t*-butyl alcohol by allowing more double-bond formation in the transition state.[6b]

Experimental Section[17]

Arylacetones.—The arylacetones were prepared from the corresponding arylacetic acids and methyllithium.[18] A 0.9 *M* solution of methyllithium in anhydrous ether was added slowly to a stirred solution of the arylacetic acid in anhydrous ether during a period of 2 hr. The reaction was stirred at room temperature for 12 hr. After addition of water and extraction with ether the organic solution was washed with water and dried, and the solvent was removed. Distillation of the residue gave 70–80% yield of the arylacetone. Phenylacetone had bp 120–122° (30 mm), lit.[19] 109–112° (24 mm); *p*-chlorophenylacetone had bp 163–165° (20 mm), lit.[20] 80–85° (0.4 mm); *m*-bromophenylacetone had bp 95–97° (0.2 mm); *p*-methylphenylacetone had bp 70–71°, lit.[21] 92–94° (3.0 mm); and *p*-methoxyphenylacetone had bp 147–148° (22 mm), lit.[22] 92–94° (3.0 mm).

1-Aryl-2-propanols.—These alcohols were prepared by lithium aluminum hydride reduction of the corresponding arylacetones. A solution of 0.09 mol of the arylacetone in 100 ml of anhydrous ether was added dropwise to a stirred solution of 0.06 mol of lithium aluminum hydride in 50 ml of anhydrous ether. The reaction was stirred for 5 hr at room temperature and quenched by addition of wet ether. After acidification and extraction with ether, the organic layer was dried and the solvent removed. The residue was distilled to give about 90% yield of the 1-aryl-2-propanol. 1-Phenyl-2-propanol had bp 127–128° (15 mm), lit.[23] 92° (2.0 mm); 1-(*p*-chlorophenyl)-2-propanol had bp 94–95° (0.1 mm); 1-(*p*-methylphenyl)-2-propanol had bp 66–67° (0.4 mm), lit.[20] 97° (2 mm); and 1-(*p*-methoxyphenyl)-2-propanol had bp 158–161° (15 mm), lit.[23] 121° (3 mm).

2-Arylpropenes.—α-Methylstyrene was purchased from Aldrich Chemical. The remaining 2-arylpropenes were prepared by dehydration of the corresponding 2-aryl-2-propanols.[24] The

(17) Melting and boiling points are uncorrected. Analyses were performed by Dr. A. Bernhardt of the Max-Planck Institute and Spang Microanalytical Laboratory, Ann Arbor, Mich. Ultraviolet spectra were determined on Cary Model 14 and Beckman DK-2A spectrophotometers.

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alcohol, 0.1–1.0 mol, was dripped slowly into a flask heated at 220° containing a powdered mixture of 6.0 g of potassium acid sulfate, 0.05 g of catechol, and 0.05 g of picric acid. Water and the 2-arylpropene were removed from the flask as they were formed by distillation at 50 mm through a 10-cm, glass-bead fractionating column. The distillate was extracted with ether, and the ether solution was dried and evaporated. The 2-arylpropenes were purified by distillation and obtained in 61–77% yield. 2-*p*-Chlorophenylpropene had bp 43–45° (1.5 mm), lit.[25] 78–80° (8 mm); 2-*m*-bromophenylpropene had bp 54–56° (0.8 mm), lit.[25] 68–72° (2 mm); 2-*p*-methylphenylpropene had bp 48–49° (3.5 mm), lit.[26] 76–78° (19 mm); and 2-*p*-methoxyphenylpropene had bp 61–62° (1.4 mm), lit.[25] 63–66° (0.5 mm).

2-Aryl-1-propanols.—These alcohols were prepared by hydroboration of the corresponding 2-arylpropenes using a modification of Brown's procedure.[27] A solution of 0.17 mol of the 2-arylpropene and 0.13 mol of sodium borohydride in 75 ml of bis(2-ethoxyethyl) ether was cooled to 0° under a nitrogen atmosphere. To this stirred solution was slowly added 0.17 mol of boron trifluoride etherate. The reaction was stirred at room temperature for 1 hr followed by the careful addition of 50 ml of 6 *M* sodium hydroxide at 0°. With continued cooling 50 ml of 30% hydrogen peroxide was added dropwise and the reaction was stirred for 1 hr at room temperature. The reaction was worked up in the usual way, and the 2-aryl-1-propanols were purified by distillation to give 85–98% yields. 2-Phenyl-1-propanol had bp 94–96° (3.5 mm); 2-(*p*-chlorophenyl)-1-propanol had bp 109–112° (0.3 mm); 2-(*m*-bromophenyl)-1-propanol had bp 92° (0.4 mm); 2-(*p*-methylphenyl)-1-propanol had bp 80° (0.4 mm), lit.[28] 102° (5 mm); and 2-(*p*-methoxyphenyl)-1-propanol had bp 95° (0.5 mm), lit.[29] 80° (0.15 mm).

2-Deuterio-2-aryl-1-propanols.—These were prepared by a modification of Sondheimer's procedure.[30] 2-Deuterio-2-(*m*-bromophenyl)-1-propanol had bp 103–106° (0.3 mm) and 2-deuterio-2-(*p*-methylphenyl)-1-propanol had bp 86–90° (0.3 mm). Their nmr spectra indicated that they were greater than 95% deuterated in the 2-position.

***p*-Toluenesulfonates.**—These were prepared by Tipson's procedure,[31] purified by crystallization from ether–pentane, and dried *in vacuo*.

1-Phenyl-2-propyl *p*-toluenesulfonate had mp 93.5–95°. *Anal.* Calcd for $C_{16}H_{18}O_3S$: C, 66.18; H, 6.25; S, 11.07. Found: C, 66.14; H, 6.14; S, 10.91.

1-(*p*-Chlorophenyl)-2-propyl *p*-toluenesulfonate had mp 79.5–80.5°. *Anal.* Calcd for $C_{16}H_{17}ClO_3S$: C, 59.16; H, 5.28; Cl, 10.92; S, 9.87. Found: C, 59.25; H, 5.31; Cl, 11.00; S, 9.99.

1-(*p*-Bromophenyl)-2-propyl *p*-toluenesulfonate had mp 57–58°. *Anal.* Calcd for $C_{16}H_{17}BrO_3S$: C, 52.04; H, 4.64; Br, 21.64; S, 8.68. Found: C, 52.08; H, 4.63; Br, 21.62; S, 8.81.

1-(*p*-Methylphenyl)-2-propyl *p*-toluenesulfonate had mp 49–50°. *Anal.* Calcd for $C_{17}H_{20}O_3S$: C, 67.08; H, 6.62; S, 10.53. Found: C, 67.17; H, 6.69; S, 10.49.

1-(*p*-Methoxyphenyl)-2-propyl *p*-toluenesulfonate had mp 77–78°. *Anal.* Calcd for $C_{17}H_{20}O_4S$: C, 63.73; H, 6.29; S, 10.01. Found: C, 63.76; H, 6.39; S, 10.01.

2-Phenyl-1-propyl *p*-toluenesulfonate had mp 50–50.5°. *Anal.* Calcd for $C_{16}H_{18}O_3S$: C, 66.18; H, 6.25; S, 11.07. Found: C, 66.33; H, 6.10; S, 11.21.

2-(*p*-Chlorophenyl)-1-propyl *p*-toluenesulfonate had mp 64.5–65°. *Anal.* Calcd for $C_{16}H_{17}ClO_3S$: C, 59.16; H, 5.28; S, 9.87. Found: C, 59.46; H, 5.46; S, 10.06.

2-(*m*-Bromophenyl)-1-propyl *p*-toluenesulfonate had mp 60.5–61°. *Anal.* Calcd for $C_{16}H_{17}BrO_3S$: C, 52.04; H, 4.64; S, 8.68. Found: C, 52.22; H, 4.77; S, 8.80.

2-Deuterio-2-(*m*-bromophenyl)-1-propyl *p*-toluenesulfonate had mp 62–63°.

2-(*p*-Methylphenyl)-1-propyl *p*-toluenesulfonate had mp 42.5–43°. *Anal.* Calcd for $C_{17}H_{20}O_3S$: C, 67.08; H, 6.62; S, 10.53. Found: C, 67.35; H, 6.71; S, 10.72.

2-Deuterio-2-(*p*-methylphenyl)-1-propyl *p*-toluenesulfonate had mp 39–40°.

2-(*p*-Methoxyphenyl)-1-propanol *p*-toluenesulfonate had mp 37–39°, lit.[29] 34–35°. *Anal.* Calcd for $C_{17}H_{20}O_4S$: C, 63.73; H, 6.29; S, 10.01. Found: C, 63.55; H, 6.23; S, 9.93.

Bromides.—These compounds were prepared by treating the corresponding *p*-toluenesulfonates with lithium bromide in acetone solution. A solution of 0.02 mol of the *p*-toluenesulfonate and 0.06 mol of anhydrous lithium bromide in 40 ml of anhydrous acetone was stirred at room temperature for 3 days. The resulting inhomogeneous mixture was poured into 100 ml of water and extracted with ether. The ether solution was dried and evaporated. The residual bromide was purified by distillation and obtained in yields of 85–95%. 1-Phenyl-2-bromopropane had bp 46–47° (0.1 mm); 1-(*p*-chlorophenyl)-2-bromopropane had bp 80–81° (0.5 mm); 1-(*m*-bromophenyl)-2-bromopropane had bp 90–91° (0.5 mm); 1-(*p*-methylphenyl)-2-bromopropane had bp 63–64° (0.3 mm); 2-phenyl-1-bromopropane had bp 50–54° (0.2 mm); 2-(*p*-chlorophenyl)-1-bromopropane had bp 72–74° (0.3 mm); 2-(*m*-bromophenyl)-1-bromopropane had bp 85–86° (0.3 mm); 2-deuterio-2-(*m*-bromophenyl)-1-bromopropane had bp 90–91° (0.8 mm); 2-(*p*-methylphenyl)-1-bromopropane had bp 55–57° (0.2 mm); 2-deuterio-2-(*p*-methylphenyl)-1-bromopropane had bp 69–70° (0.5 mm); 2-(*p*-methoxyphenyl)-1-bromopropane had bp 82–83° (0.3 mm); 2-phenyl-1-bromo-3-butene had bp 55–56° (0.9 mm).

Anhydrous Ethanol.—Absolute ethanol was refluxed with sodium and diethyl phthalate and distilled according to the method of Manske[32] to remove residual water.

Anhydrous *t*-Butyl Alcohol.—Commercial *t*-butyl alcohol (Eastman Kodak White Label) was fractionally distilled, a sharp center fraction boiling 82–82.5° (630 mm) being taken. This sample was then distilled twice from sodium.

Potassium.—Potassium metal was purified by repeated fusion in heptane. The lighter impurities floated to the surface and were skimmed off.

Second-Order Elimination Reactions.—A solution 0.02–0.06 *M* in base was prepared according to the following procedure. The bromide or *p*-toluenesulfonate (0.002–0.006 mol) was weighed into a 100-ml volumetric flask. It was dissolved in the desired amount of alcohol at room temperature and diluted to 100 ml with 0.2–0.3 *M* base solution. After shaking thoroughly 10-ml aliquots of the solution were pipetted at room temperature into 20-ml Pyrex ampoules which were then immediately immersed in ice–water and sealed. The solution in the ampoules was then equilibrated to reaction temperature.

The kinetics were measured by breaking open an ampoule, quenching the contents in ice-cold ethanol and titrating the unreacted base with standard hydrochloric acid.

For the faster elimination reactions ($k_2 > 10^{-2}$) the kinetics were measured directly from the 100-ml flask. In these cases the solution of substrate in alcohol was equilibrated to reaction temperature and then diluted to 100 ml with base solution which had also been equilibrated to reaction temperature. The solution was thoroughly shaken and requilibrated. The kinetics were measured by withdrawing 10-ml aliquots from the solution, quenching, and titrating.

Reaction rates measured using the two different methods agreed within 5%.

Substrate concentrations were determined accurately by measuring the zero and infinity point base concentrations.

The rates were calculated from each experimental point using the integrated form of the second-order rate equation. All necessary thermal expansion corrections were used. The rates were all cleanly second order.

The yields of olefins were determined by measuring the ultraviolet absorption of the last aliquot after the proper amount of dilution in 95% ethanol.

Pseudo-First-Order Elimination Reactions.—A solution approximately 0.01 *M* in the desired substrate and 0.1 *M* in the base was prepared by adding the base solution, equilibrated at the reaction temperature, to an accurately weighed sample of the substrate in 50-ml volumetric flask. The flask was immersed immediately in the constant-temperature bath and periodically shaken until the substrate had all dissolved.

Aliquots (5 ml) were then withdrawn at appropriate intervals and quenched by draining into ice-cold 95% ethanol. These solutions were immediately diluted to the proper concentrations for ultraviolet analysis.

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All the reactions were carried out under pseudo-first-order conditions and the rate constants were calculated by the use of the equation

$$k_1 = \frac{2.303}{t} \log \frac{A_\infty - A_0}{A_\infty - A_t}$$

wherein A_∞ is the measured infinity absorption, A_0 is the absorbance at $t = 0$, and A_t is the absorbance at time t. Second-order rate constants were obtained by dividing the first-order rate constant by the base concentration.

The reported rate constants from both the titrimetric and spectrophotometric runs were calculated on an IBM 7044 computer using the method of least squares. In most cases duplicate runs were measured.

Ultraviolet Spectra of 1-Aryl-1-propenes and 2-Arylpropenes.—Molar extinction coefficients measured in 95% ethanol were the following: 1-phenyl-1-propene, 18,600 (248 mμ); 1-(4-chlorophenyl)-1-propene, 24,500 (255 mμ); 1-(3-bromophenyl)-1-propene, 20,900 (253 mμ); 1-(4-methoxyphenyl)-1-propene, 22,400 (258 mμ); 2-phenylpropene, 11,400 (243 mμ); 2-(4-chlorophenyl)propane, 15,700 (248 mμ); 2-(3-bromophenyl)-propene, 10,700 (245 mμ); 2-(4-methylphenyl)propene, 13,700 (248 mμ); and 2-(4-methoxyphenyl)propene, 16,200 (257 mμ).

Registry No.—Table I (X = OTs, Y = H), 14135-71-8; Table I (X = OTs, *p*-Cl), 23430-31-1; Table I (X = OTs, *m*-Br), 23430-32-2; Table I (X = OTs, *p*-CH_3), 23430-33-3; Table I (X = OTs, *p*-OCH_3), 898-95-3; Table I (X = Br, H), 2114-39-8; Table I (X = Br, *p*-Cl), 23430-36-6; Table I (X = Br, *m*-Br), 23430-37-7; Table I (X = Br, *p*-CH_3), 2114-40-1; Table I (X = OTs, β-phenylethyl), 4455-09-8; Table I (X = Br, β-phenylethyl), 103-63-9; Table III (X = OTs, Y = *p*-H, Z = H), 23430-41-3; Table III (X = OTs, *p*-Cl, H), 23465-00-1; Table III (X = OTs, *m*-Br, H), 23430-42-4; Table III (X = OTs, *m*-Br, D), 23430-43-5; Table III (X = OTs, *p*-CH_3, H), 23430-44-6; Table III (X = OTs, *p*-CH_3, D), 23430-45-7; Table III (X = OTs, *p*-OCH_3, H), 23430-46-8; Table III (X = Br, H, H), 1459-00-3; Table III X = Br, *p*-Cl, H), 23430-48-0; Table III (X = Br, *m*-Br, H), 23430-49-1; Table III (X = Br, *m*-Br, D), 23430-50-4; Table III (X = Br, *p*-CH_3, A), 23430-51-5; Table III (X = Br, *p*-CH_3, D), 23430-52-6; Table III (X = Br, *p*-OCH_3, H), 23430-53-7.

Electronic Effects in Elimination Reactions. VII. *syn* and *anti* Eliminations of the 3-Phenyl-2-norbornyl Tosylates[1]

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The four isomeric 3-phenyl-2-norbornyl *p*-toluenesulfonates were subjected to elimination in order to study the effect of geometry on the rate. The relative rates in potassium *t*-butoxide–*t*-butyl alcohol at 50° for the four modes of elimination are *exo–syn* (*exo*-β hydrogen–*syn* elimination)/*exo–anti*/*endo–syn*/*endo–anti* = 100:3.1:0.12:0.21. The rate differences are ascribed to a combination of dihedral angle, *endo*-hydrogen removal, and *endo* leaving group effects. The Hammett ρ values for *exo–syn* and *exo–anti* are both much larger than that for an *anti*-coplanar elimination. These results imply that *syn* elimination has an inherently greater demand for carbanion character than *anti* elimination, and that noncoplanar geometry increases the electronic requirements of *anti* elimination.

The usually preferred stereochemistry for bimolecular elimination is an *anti*-coplanar relationship between the acidic hydrogen and the leaving group,[5] but *syn* pathways have been shown to compete effectively with *anti* elimination in certain rigid cyclic systems,[6] and occasionally in flexible cyclic and acyclic systems.[7] It was theorized[6] that the rate of elimination is maximized as the dihedral angle between leaving group and acidic hydrogen approaches 180° (*anti* coplanar) and 0° (*syn* coplanar). Hine[8] has given a semitheoretical justification for this concept based on the "principle of least motion" involving a mechanical model of the E2 transition state. A quantum mechanical argument has been presented by Eliel, *et al.*,[9] to show that *syn*-coplanar elimination should be less favorable than *anti*-coplanar elimination, aside from all other factors such as steric and electrostatic repulsions.

The present study of 3-phenyl-2-norbornyl tosylates is an extension of earlier work[6] on the mechanisms of *syn* and *anti* eliminations of the 2-phenylcyclopentyl tosylates, which gave the first direct comparison of electronic requirements for *syn* and *anti* eliminations in a β-phenylethyl system. The norbornyl system has the advantage of a better defined geometry in which the dihedral angles are accurately known. Cyclopentyl derivatives are more flexible, so the ground-state geometry is not necessarily the same as that for the elimination transition state.

Results

The preparation of the four isomeric 3-phenyl-2-norbornyl tosylates was recently reported by Kleinfelter.[10] The same synthetic route to *endo*-3-phenyl-

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