

Eliminations from 1-Phenyl-2-alkyl Tosylates Promoted by MeONa in MeOH. Steric Effects in Alkene-forming Elimination

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Reactions of PhCH₂CH(OTs)R [R = Me (1), Et (2), Prⁱ (3), Bu^s (4), Bu^t (5)] with MeONa in MeOH have been studied. The reactions produce both conjugated and unconjugated alkenes. The yields of the conjugated alkenes are nearly the same for 1–4, while the *E/Z* ratios depend strongly upon the α-alkyl group. The rates of eliminations forming the conjugated *E* alkenes are decreased by a bulkier alkyl group as indicated by the relative rate of 1, 0.8, 0.7, 0.6, 0.2 for 1, 2, 3, 4, 5, respectively. On the other hand, the relative rates for the formation of the unconjugated alkenes are 1, 1.7, 2.8, 1.9 for 1, 2, 3, 4, respectively, indicating that the rate increases with the double bond stabilizing ability of the alkyl groups and decreases with their steric effect. From these results, the relative steric effect of the α- and β-alkyl groups in alkene-forming elimination is assessed.

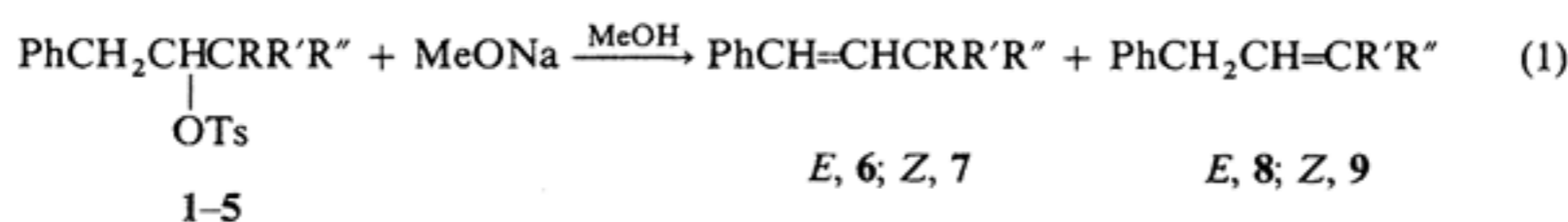
Steric effects of the β-alkyl group in alkene-forming eliminations were extensively investigated by Brown and Ingold, although their interpretation of the results were exactly opposite.^{1–4} Later, Charton reported that the steric effect was the controlling factor of the product and rate data for eliminations from RCH₂CH₂X or RCH₂CXMe₂ compounds, based upon the excellent correlation of the existing data with his steric effect parameters.⁵ Similarly, Bartsch has shown that the base steric effect in eliminations from RCH₂CHXMe compounds is strongly influenced by the β-alkyl group.⁶ In contrast, relatively little is known about the steric effect of the α-alkyl group in alkene-forming eliminations.

Very recently, we observed that the rate of eliminations from ArCH₂N(X)R compounds was decreased, and the structure of the transition state changed towards E1-like, by a bulkier *N*-alkyl group.^{7–9} To determine whether a similar effect might be operating in alkene-forming eliminations, we have investigated the reactions of PhCH₂CH(OTs)R 1–5 with MeONa in MeOH [eqn. (1)]. It has been established that alkoxide-promoted

analytical data for the new compounds were consistent with the proposed structures.

The reactions of 1–5 with MeONa in MeOH produced mixtures of isomeric alkene products. The products were identified by analysing the 500 MHz NMR spectra and the GC trace of the product mixtures and also by comparing the GC retention times with those of authentic samples. The product yields were determined with gas chromatography on a 25 m capillary column of 5% phenylsilicon. The yields of elimination product are summarized in Table 1.

The rates of reactions were followed by measuring the increase in the absorption of the conjugated alkenes at 250 or 252 nm. The rate constants were calculated by the Guggenheim method.¹¹ Excellent pseudo-first-order kinetic plots were obtained. The pseudo-first-order rate constants were divided by the base concentration to provide the second-order rate constants, which remained constant over a three-fold variation in base concentration. The second-order rate constants were multiplied by the product yields to determine the rate constants



CRR'R'' = Me (1); Et (2); Prⁱ (3); Bu^s (4); Bu^t (5)

eliminations from 2-phenylethyl tosylate proceed *via* an E1cb-like transition state.¹⁰ Since the substitution of an alkyl group at C-1 is expected to stabilize both the developing double bond and the partial positive charge at the α-carbon atom, the transition states for these reactions are expected to shift towards E2-central. Moreover, the steric requirement of the substrates can readily be modified by utilizing different α-alkyl substituents. Therefore, the steric effect of the α-alkyl group upon the alkene-forming E2 reactions may be determined by utilizing the rate and product data for the processes forming the conjugated alkenes (6 and 7). Furthermore, the relative importance of the α- and β-alkyl substituents upon the alkene-forming E2 reactions can also be assessed by comparing the data for the two competing elimination reactions forming the conjugated (6 and 7) and unconjugated alkenes (8 and 9) [eqn. (1)]. The results of these studies are reported here.

Results

Alkyl tosylates 1–5 were prepared by the reactions of appropriate 1-phenylalkan-2-ols with tosyl chloride. The spectral and

for the formation of the conjugated *E* alkenes (*k*₂). For the formation of the unconjugated alkenes, the overall rate constants were calculated by multiplying the second-order rate constants by the combined yields of 8 and 9. The *k*₂' values were then obtained by dividing the overall rate constants by the number of β-hydrogens. The rate constants are summarized in Table 2.

Relative rates of eliminations forming the conjugated *E* alkenes are 1, 0.8, 0.7, 0.6, 0.2 for 1, 2, 3, 4, 5, respectively. The influence of the α-alkyl group upon the rates correlated satisfactorily with Charton's equation using *v*' values.^{5,7,12,13} The Charton plot is shown in Fig. 1. On the other hand, the rates of eliminations forming the unconjugated alkenes increased and then decreased as the size of the β-alkyl substituent increased, as indicated by the relative rates of 1, 1.7, 2.8, 1.9 for 1, 2, 3, 4, respectively. The results indicate that both the double bond stabilizing ability and the steric effect of the alkyl groups are important in these reactions. Therefore, the rate data were correlated with log *k*₂ = α*D* + Ψ*v* + *h*, where *D* and *v* are double bond stabilizing parameters¹⁴ and Charton's steric effect parameters,^{5,7,12,13,15} respectively. Utilizing a non-linear

Table 1 Product proportions^a from elimination reactions of PhCH₂CH(OTs)R with MeONa in MeOH

R	Conjugated alkene (%)			Unconjugated alkene (%)		
	<i>E</i>	<i>Z</i>	<i>E/Z</i>	<i>E</i>	<i>Z</i>	<i>E/Z</i>
Me	75.1	7.2	10.4	17.4		
Et	71.6	6.7	10.7	15.0	6.8	2.2
Pr ⁱ	76.4	0.0		23.6		
Bu ^s	80.7	0.0		12.5	6.9	1.8
Bu ^t	100	0.0		0.0	0.0	

^a Product proportions are reproducible to $\pm 0.5\%$.

Table 2 Rate constants for elimination reactions of PhCH₂CH(OTs)R with MeONa^a in MeOH

R ^b	$k_{\text{obs}}/10^{-6} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1 \text{ c,d}}$	$k_2^{\text{overall}}/10^{-6} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1 \text{ c,d,e}}$	$k_2/10^{-6} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1 \text{ c,d,f}}$	$k_2'/10^{-7} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1 \text{ c,d,g}}$
Me	6.97	7.27	5.46 (1) ^h	4.22 (1.0) ^h
Et	6.22	6.48	4.64 (0.8) ^h	7.07 (1.7) ^h
Pr ⁱ	4.80	5.00	3.82 (0.7) ^h	11.8 (2.8) ^h
Bu ^s	3.89	4.05	3.27 (0.6) ^h	7.87 (1.9) ^h
Bu ^t	1.34	1.40	1.40 (0.2) ^h	0.00

^a [MeONa] = 0.959 mol dm⁻³. ^b [Substrate] = 2.0×10^{-5} mol dm⁻³. ^c Average of at least two kinetic runs. ^d Estimated uncertainty, $\pm 5\%$. ^e $k_2^{\text{overall}} = k_{\text{obs}}/[\text{MeONa}]$. ^f $k_2 = k_{\text{obs}} \times \text{yield of conjugated } E \text{ alkenes}/[\text{MeONa}]$. ^g $k_2' = k_{\text{obs}} \times \text{yield of unconjugated alkenes}/[\text{MeONa}] \times \text{number of } \beta\text{-hydrogens}$. ^h The numbers in parentheses are the relative rates.

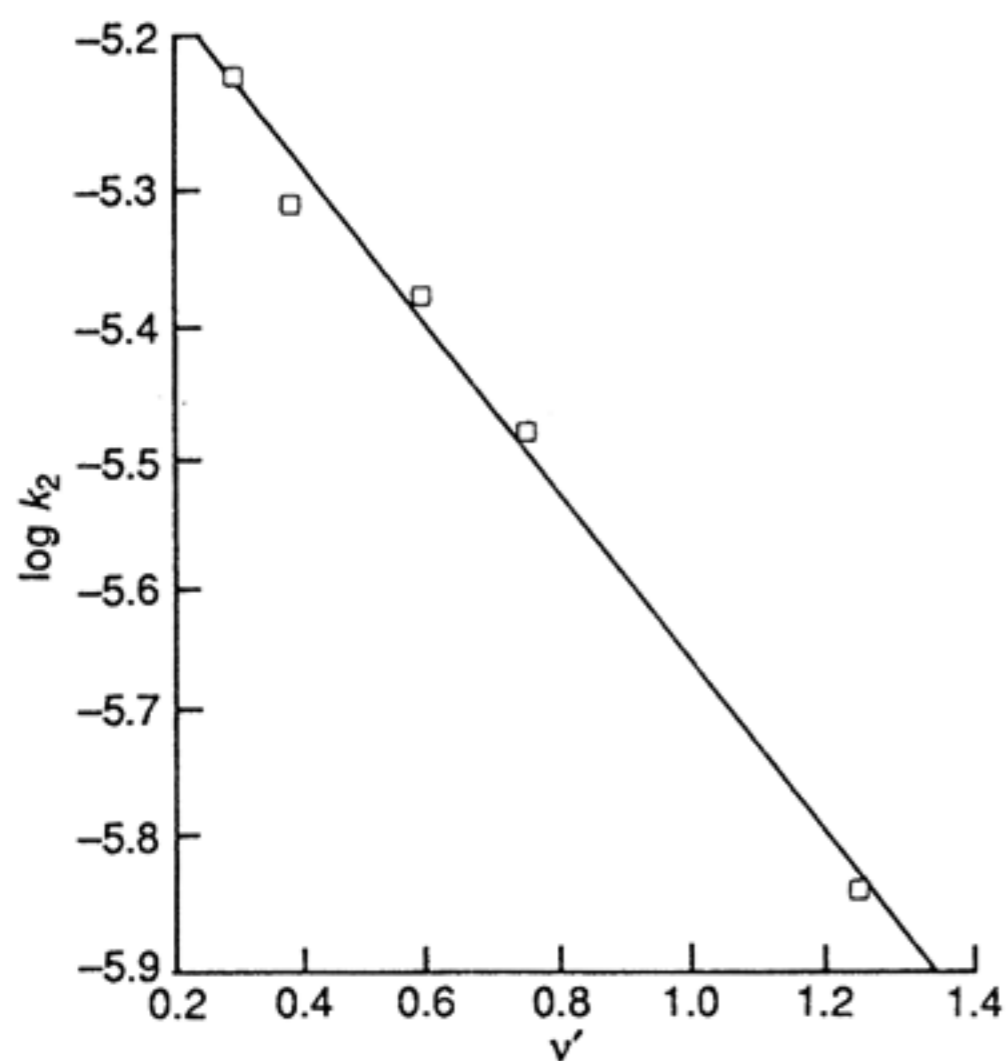


Fig. 1 Charton plot for eliminations from PhCH₂CH(OTs)R promoted by MeONa in MeOH. Slope = -0.64 , $r = 0.991$.

regression program, values of $\alpha = 0.787 \pm 0.002$ and $\Psi = -4.41 \pm 0.02$ were calculated.

Discussion

Product Distribution.—Previously it has been established that the formation of 1-alkene products in eliminations from RCH₂CHXMe (X = I, OTs) compounds is strongly favoured by a bulkier β -alkyl group owing to steric repulsion between the base and the alkyl substituent in the transition state.⁶ In contrast, the yield of the conjugated alkenes changes only slightly with the variation of the α -alkyl groups (Table 1). The yield decreases with the change of the alkyl group from Me to Et, apparently owing to the increased stabilization of the unconjugated alkene product from **2** by the methyl group. The yields are nearly the same for **2** and **3**, probably because the double bond stabilizing ability of the two methyl groups at C-2 in 2-methyl-4-phenylbut-2-ene is counterbalanced by their steric effect. When the stability of the unconjugated products is

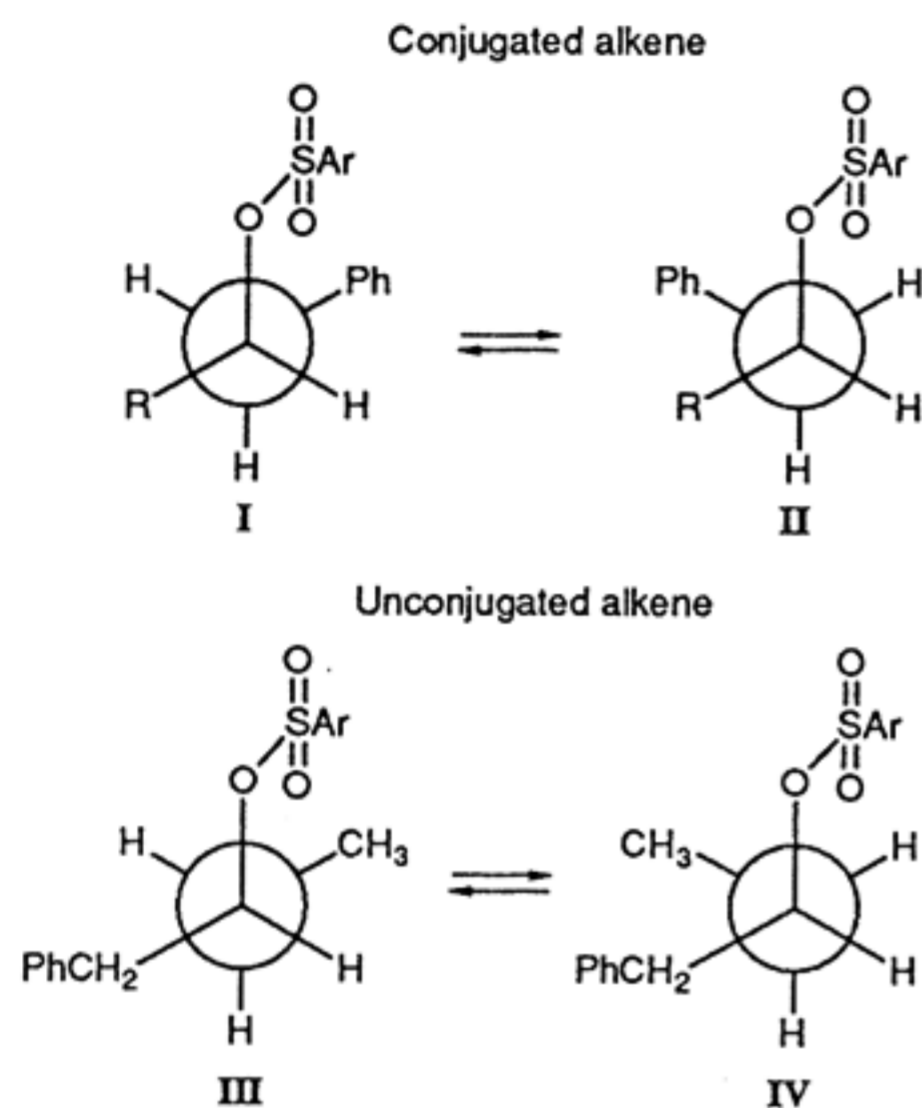
kept constant, the alkyl group steric effect becomes evident as indicated by the higher yield of **6** from **4** than from **3**. It appears that the product distribution of these reactions is determined by both double bond stabilizing ability and the steric effect of the alkyl groups. The result is in contrast to the regiospecific formation of the conjugated imines in eliminations from closely-related PhCH₂N(OAs)R compounds under the same conditions.⁹ Thus the stabilization of the partial double bond by conjugation with the phenyl group must be less important in the alkene- than in the imine-forming transition state.

On the other hand, the *E/Z* ratios depend strongly on the substrate steric effect. The (*E*)- to (*Z*)-1-phenylpropene ratio for **1** is 10, which is much smaller than the ratio of 23.5 determined for the reactions of 1-phenyl-2-propyl chloride with MeONa in MeOH at 60 °C.¹⁶ The result may be attributed to the leaving group steric effect. Since the bulky tosylate leaving group is expected to prefer a conformation where the sulfur is *anti* to the α -alkyl group,^{17a} it should be more destabilized than when such interaction is absent (Fig. 2). This would predict a lower *E/Z* ratio for the former, as observed. The ratios are nearly the same for **1** and **2** owing to the similarity in the steric requirement of the Me and Et groups.¹⁵ However, the ratio increased sharply to infinity with further increase in the steric bulk as indicated by the zero yield of the *Z* product from **3–5** (Table 1). Assuming *anti* transition states for all of these eliminations, the results can be attributed to the higher concentration of the *anti* (**I**) than the *gauche* (**II**) conformers of **1–5** and the lower free energy of activation for the reactions leading to the *E* products **6** for the sterically more congested substrates (Fig. 2). The much lower *E/Z* ratio for the unconjugated alkene products from **2** than for the conjugated alkene products from **1** can also be explained similarly by assuming a smaller steric requirement for the benzyl than the phenyl group in these reactions.¹⁵ However, the smaller ratio of 1.8 for the 2-methyl-5-phenylpent-3-ene products from **4** does not indicate the steric effect, but simply reflects the diastereomeric ratio of the reactant mixture, because each diastereomer can produce only one product.

Relative Rates of Alkene- and Imine-forming Eliminations.—The second-order rate constants for eliminations forming *E* conjugated alkenes from **1–5** are $1.40\text{--}5.46 \times 10^{-6} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Table 2). The rates are approximately 10^5 times slower than

Table 3 Susceptibilities of various elimination reactions to steric effects

Reaction	Ψ or Ψ'	Reference
$RCH_2CH_2N^+Me_3 + EtO^- \xrightarrow{EtOH} RCH=CH_2$	-2.36	5
$RR'CHCH(OTs)CH_2Ph + MeO^- \xrightarrow{MeOH} RR'CH=CHCH_2Ph$	-4.41	This work
$PhCH_2CH(OTs)R + MeO^- \xrightarrow{MeOH} PhCH=CHR$	-0.64	This work
$PhCH_2N(Cl)R + MeO^- \xrightarrow{MeOH} PhCH=NR$	-2.11	7
$PhCH_2N(OAs)R + MeO^- \xrightarrow{MeOH} PhCH=NR$	-0.71	9

**Fig. 2** Possible conformers of compounds 1-5

those of the closely-related imine-forming eliminations from $PhCH_2N(OAs)R$ compounds under the same conditions.⁹ The difference is much greater than the 5×10^3 fold retardation in rate for eliminations from $PhCH_2CH(Cl)Me$ compared with $PhCH_2N(Cl)Me$ under similar conditions.¹⁸ Considering that the $C-OSO_2Ar$ bond is approximately 50 kcal mol^{-1} * stronger than the $N-OSO_2Ar$ bond and the $C-Cl$ bond is only 20 kcal mol^{-1} stronger than the $N-Cl$ bond,¹⁹ the result can be attributed to the greater difference in the strength of the bonds to the leaving group for the former.

Steric Effects.—The rates of eliminations from 1-5 decrease systematically as the steric requirement of the α -alkyl group is increased. The relative rates of eliminations from 1-5 to afford 6 are 1, 0.8, 0.7, 0.6, 0.2 for 1, 2, 3, 4, 5, respectively. When $\log k_2$ for the formation of 6 was plotted against Charton's ν' values,^{12,13} a straight line was obtained with excellent correlation (Fig. 1). As shown previously, the result can be interpreted in terms of the repulsive interaction between the base and the α -alkyl group in the transition state.⁷⁻⁹ On the other hand, the relative rates of eliminations forming the unconjugated alkenes are 1, 1.7, 2.8, 1.9 for 1, 2, 3, 4, respectively, indicating that the rate increases with increased branching at the β -carbon and then decreases. Moreover, the data could be correlated with the modified Charton's equation, $\log k_2 = \alpha D + \Psi \nu + h$, to give $\alpha = 0.787 \pm 0.002$ and $\Psi = -4.41 \pm 0.02$, respectively. This result clearly demonstrates that the alkyl groups influence the elimination rates not only by the

steric effect but also by the double bond stabilizing ability. The increase in the rates with increased branching at the β -carbon is consistent with the assumption that these reactions proceed *via* an E2-central transition state.

The susceptibilities of various eliminations to alkyl group steric effect under comparable conditions are summarized in Table 3. The Ψ' value for eliminations from $PhCH_2CH(OTs)R$ is much smaller than those for the $RR'CHCH(OTs)CH_2Ph$ and $RCH_2CH_2N^+Me_3$ compounds, indicating that the steric effect of the α -alkyl group is smaller than that of the β -alkyl group. The result is consistent with that observed in the product studies (*vide supra*) and can readily be understood by considering the longer distance from the base to the α - than to the β -alkyl group in the transition state. The greater steric effect of the β -alkyl group in eliminations from $RR'CHCH(OTs)CH_2Ph$ than from $RCH_2CH_2N^+Me_3$ compounds may be attributed to the greater double bond character and the greater steric requirement at the α -carbon in the former transition state. Since the former transition state should have less negative charge development at the β -carbon^{17b} and the developing double bond can be more stabilized by the β -alkyl groups, the β -carbon atom is expected to have more sp^2 character. This would decrease the distance between the approaching base and the β -substituent and thus increase the steric repulsion between them.²⁰ Moreover, the presence of the benzyl group at the α -carbon atom would provide additional congestion in the former transition state. Therefore, the sensitivity of the elimination reactions to the substrate steric effect must be greater for the former.

It is interesting to note that the steric effect in eliminations from $PhCH_2CH(OTs)R$ is similar to that of $PhCH_2N(OAs)R$ even though the structures of the transition states are quite different. From previous work, the smaller steric effect observed in eliminations from $PhCH_2N(OAs)R$ than from $ArCH_2N(Cl)R$ has been attributed to the looser transition state for the former.⁹ The smaller steric effect of the α -alkyl group upon the eliminations from 1-5 than from *N*-chloramine can also be explained similarly. Since the $C=N$ bond is shorter than the $C=C$ bond and the imine-forming transition state is known to have extensive double bond character,²¹ the distance between the base and the α -alkyl group is expected to be greater in the alkene-forming transition state. Therefore, the sensitivity of the elimination reaction to the substrate steric effect must be smaller for the former.

The present result demonstrates that the alkyl substituents influence the elimination reactions by both steric and double bond stabilizing effects and that the steric effect of the β -alkyl group is greater than that of the α -alkyl group in alkene-forming eliminations that proceed *via* an E2-central transition state.

Experimental

Materials.—1-Phenyl-2-alkyl tosylates 1-5 were prepared by the reactions of appropriate 1-phenyl-2-alkyl alcohols and tosyl chloride.²² The physical, spectral and analytical data

* 1 cal = 4.184 J.

revealed that these compounds were racemic mixtures except that **4** was a mixture of diastereomers with a 1.9 to 1 ratio. The melting points ($^{\circ}\text{C}$), IR (KBr, SO_2 , cm^{-1}), NMR (CDCl_3), and analytical data of these compounds are as follows: $\text{PhCH}_2\text{CH}(\text{OTs})\text{Me}$, 1-phenyl-2-propyl tosylate (**1**), m.p. 90; ν_{max} 1140, 1340; δ_{H} 1.3 (d, 3 H), 2.4 (s, 3 H), 2.8 (q, 1 H), 2.9 (q, 1 H), 4.7 (sextet, 1 H), 7.0–7.2 (m, 7 H), 7.6 (d, 2 H) (Found: C, 66.55; H, 6.5; S, 11.2. Calc. for $\text{C}_{16}\text{H}_{18}\text{O}_3\text{S}$: C, 66.18; H, 6.25; S, 11.04); $\text{PhCH}_2\text{CH}(\text{OTs})\text{Et}$, 1-phenyl-2-butyl tosylate (**2**), m.p. 54; ν_{max} 1140, 1340; δ_{H} 0.8 (t, 3 H), 1.6 (m, 2 H), 2.4 (s, 3 H), 2.9 (m, 2 H), 4.6 (quintet, 1 H), 7.0–7.2 (m, 7 H), 7.7 (d, 2 H) (Found: C, 67.0; H, 6.9; S, 10.8. Calc. for $\text{C}_{17}\text{H}_{20}\text{O}_3\text{S}$: C, 67.08; H, 6.62; S, 10.53); $\text{PhCH}_2\text{CH}(\text{OTs})\text{Pr}^i$, 3-methyl-1-phenyl-2-butyl tosylate (**3**), m.p. 81; ν_{max} 1140, 1340; δ_{H} 0.9 (q, 6 H), 1.9 (m, 1 H), 2.4 (s, 3 H), 2.9 (d, 2 H), 4.6 (sextet, 1 H), 7.0–7.3 (m, 7 H), 7.6 (d, 2 H) (Found: C, 68.2; H, 7.3; S, 10.2. Calc. for $\text{C}_{18}\text{H}_{22}\text{O}_3\text{S}$: C, 67.90; H, 6.96; S, 11.07); $\text{PhCH}_2\text{CH}(\text{OTs})\text{Bu}^s$, 4-methyl-1-phenyl-2-pentyl tosylate (**4**), m.p. 65; ν_{max} 1140, 1340; δ_{H} 0.7–1.9 (m, 9 H), 2.4 (d, 2 H in 1.9:1 ratio), 2.8 (q, 1 H), 2.9 (q, 1 H), 4.7 (m, 1 H), 7.0–7.3 (m, 7 H), 7.5 (d), 7.6 (d, 2 H in 1.9:1 ratio) (Found: C, 69.3; H, 7.6; S, 9.65. Calc. for $\text{C}_{19}\text{H}_{24}\text{O}_3\text{S}$: C, 68.85; H, 7.30; S, 9.67); $\text{PhCH}_2\text{CH}(\text{OTs})\text{Bu}^t$, 3,3-dimethyl-1-phenyl-2-butyl tosylate (**5**), m.p. 96; ν_{max} 1140, 1340; δ_{H} 1.0 (s, 9 H), 2.3 (s, 3 H), 2.7 (quartet, 1 H), 3.0 (quartet, 1 H), 4.8 (quartet, 1 H), 7.0–7.1 (m, 7 H), 7.4 (d, 2 H) (Found: C, 68.9; H, 7.7; S, 9.9. Calc. for $\text{C}_{19}\text{H}_{24}\text{O}_3\text{S}$: C, 68.85; H, 7.30; S, 9.67).

Product Studies.—The products of eliminations from **1–5** were obtained by reacting approximately 0.5 g of the substrates with 1.0 mol dm^{-3} MeONa in MeOH for 2 days at room temperature. The products were isolated by extracting the mixture with hexane. The hexane solution was analysed with gas chromatography on a 25 m capillary column of 5% phenylsilicon at 60–80 $^{\circ}\text{C}$. The products were identified by analysing the NMR spectra of the product mixtures. All of the NMR peaks were nicely separated in the 500 MHz NMR spectrum and thus could be assigned to each product. The relative peak intensities observed in the NMR spectra were then matched with those in the GC trace. To confirm the validity of this method, authentic mixtures of *Z* and *E* conjugated alkenes were synthesized by the Wittig reactions of $\text{Ph}_3\text{P}=\text{CHPh}$ with appropriate aldehydes. The GC retention time of the authentic samples were exactly the same as those of the product mixtures assigned by the above method.

Kinetic Studies.—Reactions of **1–5** with MeONa–MeOH were followed using a UV spectrophotometer with thermostatted cuvette holders under pseudo-first-order conditions employing at least a tenfold excess of base. Reactions were initiated by injecting 5–10 mm^3 of *ca.* $10^{-2} \text{ mol dm}^{-3}$ solution of the substrate in MeOH into a cuvette containing 3.0 cm^3 of MeONa–MeOH. Cuvettes were temperature equilibrated for at least 20 min prior to a kinetic run. The increase in the absorption of the conjugated alkenes at 250 or 252 nm was monitored for the initial period and then after three half-lives. The cuvettes were always kept in a constant temperature bath when the measurement was not made. The rate constants were calculated by the Guggenheim method.¹¹ Excellent pseudo-first-order kinetic plots were obtained. The pseudo-first-order

rate constants were divided by the base concentration to provide the second-order rate constants, which remained constant for a five-fold variation in base concentration. The k_2 values were calculated by multiplying the second-order rate constants by the yields of conjugated *E* alkenes. The k_2' values were obtained by dividing the overall rate constants for the unconjugated alkenes, respectively.

Control Experiment.—The possibility of isomerization of the alkene products under the reaction conditions was assessed by determining the product ratios periodically with gas chromatography as described above. When the products were extracted with hexane before the reaction was completed the hexane solution contained small amounts of the tosylates, which interfered with the GC analysis. The hexane solution was cooled to -60°C in a freezer, filtered to remove the tosylate, and concentrated by bubbling with nitrogen when necessary. The product distribution was always within experimental error over a 1–9 day period.

Acknowledgements

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