Orientation in Base-Promoted 1,2-Elimination Reactions. Influence of β-Alkyl and Leaving Groups upon the Threshold for Base Steric Effects[1]

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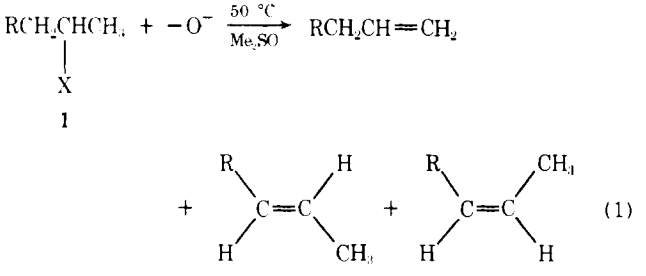
Abstract: Orientation is reported for eliminations from 2-butyl iodide and tosylate, 4-methyl-2-pentyl iodide and tosylate, and 4,4-dimethyl-2-pentyl tosylate promoted by oxy anion bases in dimethyl sulfoxide. The level of base complexity which is necessary for the onset of base steric effects is influenced by the β-alkyl group, but not the leaving group. A syn elimination pathway is apparent for the formation of *trans*-4,4-dimethyl-2-pentene from 4,4-dimethyl-2-pentyl tosylate.

Introduction

Assessing the influence of base strength and size upon orientation for olefin-forming elimination reactions has been a subject of active research interest for nearly 3 decades.[3,4] Once the complicating effects of base association in solvents of low polarity were recognized,[5] it was convincingly demonstrated[6,7] that base strength, not size, controls positional orientation. Thus, for eliminations from 2-iodobutane induced by oxy anion bases in dimethyl sulfoxide (Me_2SO), linear relationships were noted for free-energy differences between transition states for formation of terminal and internal olefins, $\Delta\Delta G^{\ddagger}$ (1-butene-*trans*-2-butene) or $\Delta\Delta G^{\ddagger}$ (1-butene-*cis*-2-butene), and pK_a for the conjugate acid of the bases (see Figure 1, circles). Divergence from these linear free energy relationships was only observed with the outsized bases 2,6-di-*tert*-butyl phenoxide (system 11), tricylohexylmethoxide (system 17), and tri(2-norbornyl)methoxide (system 18). For these highly ramified bases, a larger proportion of 1-butene was realized than had been anticipated on the basis of base strength. This divergence was due to the onset of a superimposed steric effect of the base which favored removal of the accessible methyl hydrogen rather than a more shielded methylene hydrogen (eq 1).



In order to investigate the effects of alkyl group structure (R in **1**) and leaving group identity upon the level of base complexity necessary to reach the threshold for base steric interactions, we have determined orientation for eliminations from 2-butyl iodide and tosylate, 4-methyl-2-pentyl iodide and tosylate, and 4,4-dimethyl-2-pentyl tosylate induced by a variety of oxy anion bases in Me_2SO at 50 °C.

Results

Elimination reactions of the alkyl iodides and tosylates with oxy anion bases in Me_2SO were conducted using a nitrogen gas sweep procedure[8] to carry the evolved olefins into a receiver trap. Control experiments demonstrated that the product alkenes were not isomerized by the base under these conditions.

The relative proportions of isomeric alkenes produced in eliminations from 2-butyl iodide (**2**), 4-methyl-2-pentyl iodide (**3**), 2-butyl tosylate (**4**), 4-methyl-2-pentyl tosylate (**5**), and 4,4-dimethyl-2-pentyl tosylate (**6**), induced by alkoxides, phenoxides, and carboxylates in Me_2SO at 50 °C are recorded in Tables I–V. Literature values for the pK_as of the conjugate acids of the oxy anion bases in Me_2SO are also collected in the tables.

Appropriate control experiments demonstrated that negligible amounts of olefinic products arose from solvolysis of the substrates under conditions used for the base-promoted elimination reactions. For the iodides, even such weak bases as *p*-nitrobenzoate (pK_a = 8.9),[13] *p*-nitrophenoxide (pK_a = 11.0),[13] and benzoate (pK_a = 11.0)[13] could be utilized. However, for the tosylates, *p*-aminobenzoate (pK_a = 12.7)[13] was the weakest base that could be employed without significant concomitant solvolysis. This indicates that the reported orientation[10] for reactions of 2-butyl tosylate with *o*- and *p*-nitrophenoxide in Me_2SO at 55 °C probably includes contributions from both solvolytic and base-promoted reaction pathways.

Orientation for the solvolytic eliminations from **2, 4,** and **5** in Me_2SO was determined at 50 °C in the presence of 2,6-lutidine (sterically hindered base present to prevent acid-catalyzed solvolysis or olefin isomerization). Results are entered as systems 20 (Table I), 41 (Table III), and 57 (Table V).

Equilibration of 4,4-dimethyl-1-pentene or *trans*-4,4-dimethyl-2-pentene with *t*-BuOK–Me_2SO at 50 °C gave the relative olefinic percentages presented in system 58 (Table V).

Plots of $\Delta\Delta G^{\ddagger}$(1-alkene-*trans*-2-alkene) vs. pK_as of the conjugate acids of the oxy anion bases in Me_2SO for eliminations from **2** and **4, 3, 5,** and **6** are given in Figures 1–4, respectively.

Discussion

In order to suppress the complicating effects of base association upon orientation in eliminations from secondary alkyl halides and tosylates, Me_2SO was chosen as the reaction solvent.[5] Evidence that dissociated oxy anion bases are the effective base species in these eliminations is provided by the insensitivity of orientation to the nature of the *tert*-butoxide counterion in reactions with **2** (systems 1–3, Table I). Variation of the cation from potassium to potassium in the presence of 18-crown-6 to sodium produced the same orientation within experimental error.

Tables I–V present a wealth of data for olefinic product distributions in reactions of secondary alkyl halides and tosylates promoted by dissociated anionic bases in Me_2SO. A total of 48 combinations of alkyl group, leaving group, and oxy anion

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base are included. Prior to the discussion of this collected orientation data, the mechanism and stereochemistry of these eliminations must be considered.

Mechanism and Stereochemistry

Base-promoted eliminations from simple alkyl halides and tosylates are the least controversial examples of the concerted E2 mechanism.[14,15] For these substrates, carbanion mechanisms are rendered unlikely owing to the low acidity of the β hydrogens. Since control experiments rule out solvolytic elimination, it seems most reasonable that these reactions proceed via the E2 mechanism.

Stereospecific anti eliminations have been reported for reactions of 2-butyl-*3-d* bromide[16] and tosylate[17] with *t*-BuOK-Me_2SO. Therefore, an anti stereochemistry is certain for eliminations from **2** and **4** and seems highly likely for **3** and **5**. As will be amplified later, the congested structure of **6** makes its elimination stereochemistry far less certain.

Effect of Alkyl Group for Alkyl Iodides

As previously mentioned, linear free energy relationships exist between positional orientation and oxy anion base strength for eliminations from **2** (Figure 1, circles). With the highly ramified bases 2,6-di-*tert*-butylphenoxide (system 11), tricyclohexylmethoxide (system 17), and tri(2-norbornyl)-methoxide (system 18), base steric effects become important and the correlation between positional orientation and base strength is broken.

The effect of changing the substrate from **2** to **3** (replacement of R = Me to R = *i*-Pr in **1**) upon the threshold of base steric interactions is readily evident in Figure 2. Base steric effects are now apparent for *tert*-butoxide (system 21) in addition to 2,6-di-*tert*-butylphenoxide (system 26), tricyclohexylmethoxide (system 31), and tri(2-norbornyl)methoxide (system 32). Thus, the threshold for base steric interactions in the removal of a methylene hydrogen from **1** occurs with bases of lesser complexity when R = *i*-Pr than if R = Me.

Using vertical displacement of points from the line as a measure of steric hindrance in these elimination reactions, the base spatial demands increase: *tert*-butoxide < tricyclohexylmethoxide < tri(2-norbornyl)methoxide < 2,6-di-*tert*-butylphenoxide.

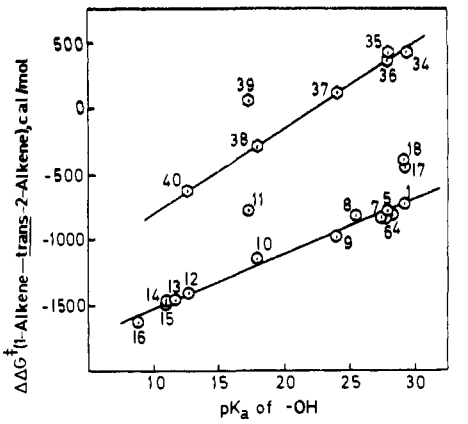


Figure 1. Plot of free-energy difference for formation of 1-butene and *trans*-2-butene from 2-butyl iodide (circles) or from 2-butyl tosylate (hexagons) vs. the pK_a of the conjugate acid of the base. System numbers refer to Tables I and III.

Since *t*-BuOK-Me_2SO is an often encountered base-solvent combination for elimination reactions and the level of substrate complexity present in **3** is similar to that of many common substrates, it is clear that even in Me_2SO *tert*-butoxide will exhibit both base strength and steric properties in most eliminations. This complicating factor was not recognized in earlier work when orientation differences in eliminations induced by EtOK-EtOH and *t*-BuOK-DMF were ascribed only to the higher base strength of the latter.[18]

Comparison of orientation data in Table II for bases of similar strength reveals that the enhanced proportions of 4-methyl-1-pentene observed with sterically hindered bases result from decreases in the relative proportions of both *trans*- and

Table I. Relative Olefinic Proportions[a] from Reactions of 2-Butyl Iodide with Oxy Anion Bases in Dimethyl Sulfoxide at 50.0 °C

system	base	pK_a of conjugate acid in Me_2SO	% 1-butene	*trans*-2-butene: *cis*-2-butene
1[b]	potassium *tert*-butoxide	29.2,[c] 29.4[d]	19.7	3.10
2[b,e]	potassium *tert*-butoxide		19.0	3.01
3[b]	sodium *tert*-butoxide		18.3	3.32
4[f]	disodium ethylene glycolate	28.4[d]	17.6	3.12
5[g]	sodium *n*-propoxide	28.0,[c] 27.9[d]	18.5	3.34
6[g]	sodium ethoxide	27.4,[c] 28.2[d]	17.1	3.31
7[g]	sodium methoxide	27.0,[c] 27.9[d]	17.0	3.14
8[f]	sodium triphenylmethoxide	25.5[d]	17.7	3.20
9[g]	sodium 2,2,2-trifluoroethoxide	24.0[d]	14.3	3.32
10[g]	potassium phenoxide	18.0[h]	11.4	3.34
11[g]	potassium 2,6-di-*tert*-butylphenoxide	17.3[h]	19.2	3.70
12[g]	potassium *p*-aminobenzoate	12.7[c]	8.0	3.42
13[g]	potassium acetate	11.6[c]	7.4	3.47
14[g]	potassium *p*-nitrophenoxide	11.0[h,i]	7.5	3.58
15[g]	potassium benzoate	11.0[c]	7.2	3.24
16[g]	potassium *p*-nitrobenzoate	8.9[c]	5.8	3.51
17[j]	potassium tricyclohexylmethoxide	(29)[k]	27.2	3.04
18[j]	potassium tri(2-norbornyl)methoxide	(29)[k]	29.4	3.41
19[l]	potassium *tert*-butoxide (in *tert*-butyl alcohol)		29.9	2.09
20[m]	solvolysis		4.0	3.57

[a] Olefinic percentages are reproducible to ±1%. [b] [2-BuI] = 0.10 M, [base] = 0.25 M. [c] Ritchie, C. D. In "Solute-Solvent Interactions", Coetzee, J. F.; Ritchie, C. D., Eds.; Marcel Dekker: New York, 1969; p 230. [d] Arnett, E. M.; Small, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 808-816. [e] 18-Crown-6 (0.25 M) present. [f] Data from ref 7. [g] Data from ref 6. [h] Bordwell, F. G. EUCHEM Conference on Mechanisms of Elimination Reactions, Assisi, Italy, Sept 1977. [i] Kolthoff, T. M.; Chantooni, M. K.; Bhownik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23-28. [j] Data from ref 9. [k] pK_a assumed to be the same as that of *tert*-butoxide. [l] [2-BuI] = 0.10 M, [base] = 0.50 M. [m] In Me_2SO, in the presence of 2,6-lutidine.

Table II. Relative Olefinic Proportions[a] from Reactions of 4-Methyl-2-pentyl Iodide with Oxy Anion Bases in Dimethyl Sulfoxide at 50.0 °C

system	base	pK_a[b]	% 4-methyl-1-pentene	% *trans*-4-methyl-2-pentene	% *cis*-2-methyl-2-pentene
21[c]	potassium *tert*-butoxide	29.3	38.7	59.7	1.6
22[d]	sodium *n*-propoxide	28.0	24.5	72.8	2.7
23[d]	sodium ethoxide	27.8	21.9	75.4	2.7
24[d]	sodium 2,2,2-trifluoroethoxide	24.0	17.8	79.1	3.1
25[c]	potassium phenoxide	18.0	13.6	82.9	3.5
26[c]	potassium 2,6-di-*tert*-butylphenoxide	17.3	51.4	46.5	2.1
27[d]	sodium *p*-aminobenzoate	12.7	7.4	87.7	4.9
28[d]	sodium *p*-nitrophenoxide	11.0	7.4	88.4	4.2
29[d]	sodium benzoate	11.0	5.9	89.0	5.1
30[d]	sodium *p*-nitrobenzoate	8.9	4.5	90.4	5.1
31[d]	potassium tricyclohexylmethoxide	(29)	58.3	39.6	2.1
32[d]	potassium tri(2-norbornyl)-methoxide	(29)	66.1	31.8	2.1
33[d]	potassium *tert*-butoxide (in *tert*-butyl alcohol)[e]		82.3	16.1	1.6

[a] Olefin percentages were reproducible to ±1.0%. [b] pK_a of conjugate acid of the base in Me_2SO. See Table I for references. [c] [RI] = 0.10 M, [base] = 0.25 M. [d] [RI] = 0.40 M, [base] = 0.50 M or saturated solution. [e] Ampule technique.

Table III. Relative Olefinic Proportions[a] from Reactions[b] of 2-Butyl Tosylate with Oxy Anion Bases in Dimethyl Sulfoxide at 50.0 °C

system	base	pK_a[c]	% 1-butene	% *trans*-2-butene	% *cis*-2-butene
34[d]	potassium *tert*-butoxide	29.3	58.5	29.0	12.5
35	potassium *n*-propoxide	28.0	57.8	29.5	12.7
36[e]	potassium ethoxide	27.8	56.0	31.1	12.9
37	potassium 2,2,2-trifluoroethoxide	24.0	46.0	37.2	16.8
38[f,g]	potassium phenoxide	18.0	30.6	46.2	23.1
39	potassium 2,6-di-*tert*-butylphenoxide	17.3	40.9	36.2	22.9
40	potassium *p*-aminobenzoate	12.7	20.0	52.1	27.9
41[h]	solvolysis		20.0	52.0	34.0
42[i]	equilibrium		9	64	27

[a] Olefin percentages were reproducible to ±1%. [b] [ROTs] = 0.10 M, [base] = 0.25 M. [c] pK_a of conjugate acid of the base in Me_2SO. See Table I for references. [d] Reference 10 reports 61% 1-butene, 28% *trans*-2-butene, and 11% *cis*-2-butene at 55 °C. [e] Reference 10 reports 54% 1-butene, 32% *trans*-2-butene, and 14% *cis*-2-butene at 55 °C. [f] Reference 10 reports 31% 1-butene, 46% *trans*-2-butene, and 23% *cis*-2-butene at 55 °C. [g] [PhOH] = 0.06 M. [h] In Me_2SO, in the presence of 2,6-lutidine. [i] Equilibration with *t*-BuOK–Me_2SO at 55 °C, ref 11.

Table IV. Relative Olefinic Proportions[a] for Reactions[b] of 4-Methyl-2-pentyl Tosylate with Oxy Anion Bases in Dimethyl Sulfoxide at 50.0 °C

system	base	pK_a[c]	% 4-methyl-1-pentene	% *trans*-4-methyl-2-pentene	% *cis*-4-methyl-2-pentene
43	potassium *tert*-butoxide	29.3	82.5	15.0	2.5
44	potassium *n*-propoxide	28.0	67.3	28.4	4.3
45	potassium ethoxide	27.3	62.7	32.7	4.6
46	potassium 2,2,2-trifluoroethoxide	24.0	50.2	43.3	6.5
47	potassium phenoxide	18.0	34.6	54.6	10.8
48	potassium 2,6-di-*tert*-butylphenoxide	17.3	70.2	21.7	8.1
49[d]	equilibrium		3	83	14

[a] Olefinic percentages were reproducible to ±1%. [b] [ROTs] = 0.10 M; [base] = 0.25 M. [c] pK_a of conjugate acid of the base in Me_2SO. See Table I for references. [d] Equilibration with *t*-BuOK–Me_2SO at 55 °C, ref 12.

Table V. Relative Olefinic Proportions[a] for Reactions[b] of 4,4-Dimethyl-2-pentyl Tosylate with Oxy Anion Bases in Dimethyl Sulfoxide at 50.0 °C

system	base	pK_a[c]	% 4,4-dimethyl-1-pentene	% *trans*-4,4-dimethyl-2-pentene	% *cis*-4,4-dimethyl-2-pentene
50	potassium *tert*-butoxide	29.3	65.5	34.5	0
51	potassium *n*-propoxide	28.0	43.6	56.4	0
52	potassium ethoxide	27.8	41.1	58.9	0
53	potassium 2,2,2-trifluoroethoxide	24.0	31.6	68.4	0
54	potassium phenoxide	18.0	21.6	77.8	0.6
55	potassium 2,6-di-*tert*-butylphenoxide	17.3	55.6	43.3	1.1
56	potassium *p*-aminobenzoate	12.7	11.8	86.0	2.2
57[d]	solvolysis		8.2	82.1	9.7
58[e]	equilibrium		5.4	94.6	0

[a] Olefinic percentages were reproducible to ±1%. [b] [ROTs] = 0.10 M, [base] = 0.25 M. [c] pK_a of conjugate acid of the base in Me_2SO. See Table I for references. [d] In Me_2SO, in the presence of 2,6-lutidine. [e] Equilibration with *t*-BuOK–Me_2SO at 50 °C (see Experimental Section).

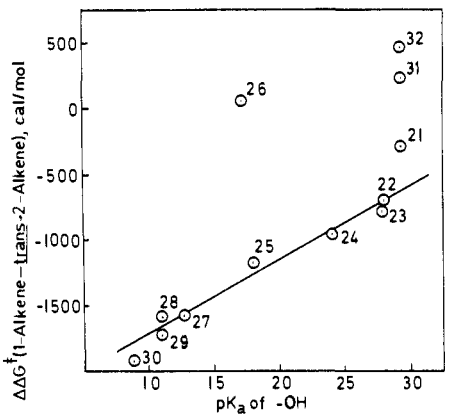


Figure 2. Plot of free-energy difference for formation of 4-methyl-1-pentene and *trans*-4-methyl-2-pentene from 4-methyl-2-pentyl iodide vs. the pK_a of the conjugate acid of the base. System numbers refer to Table II.

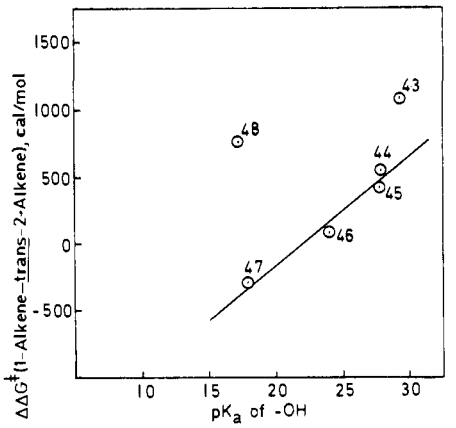
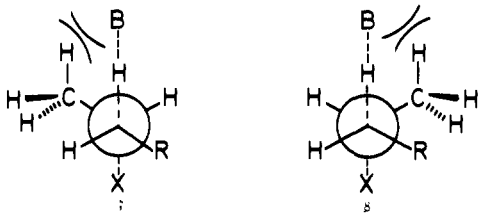


Figure 3. Plot of free-energy difference for formation of 4-methyl-1-pentene and *trans*-4-methyl-2-pentene from 4-methyl-2-pentyl tosylate vs. the pK_a of the conjugate acid of the base. System numbers refer to Table IV.

cis-4-methyl-2-pentene. This destabilization would appear to result from steric repulsion between the base and α- or β-alkyl groups in transition states for internal olefin formation **7** and **8**. In the corresponding transition state for terminal alkene



production, the base has much more freedom to assume positions which minimize such interactions.

Although positional orientation in eliminations from **3** is more sensitive to steric effects of dissociated bases than previously observed with **2**, associated bases such as *t*-BuOK-*t*-BuOH (system 33, Table II) still yield more terminal alkene than does any dissociated base.[9]

The line slope in Figure 2 is somewhat greater than that for 2-butyl iodide in Figure 1. Therefore, positional orientation is slightly more sensitive to change in base strength for eliminations from **3** than from **2**. For both substrates, the positive line slopes signify an increase in the relative proportion of 1-alkene over *trans*-2-alkene as base strength is enhanced.

In order to probe the influence of an even larger R group in **1** upon the threshold for base steric effects, the synthesis of 4,4-dimethyl-2-pentyl iodide (**1**, R = *t*-Bu) was attempted. However, these efforts were unsuccessful and attention was shifted to a corresponding tosylate series of 2-butyl, 4-methyl-2-pentyl, and 4,4-dimethyl-2-pentyl tosylates **4–6**, respectively. In addition to alkyl group variation, this series allows for a comparison of the symmetrical iodo leaving group with the dissymmetrical tosyloxy leaving group.

Effect of Alkyl Group for Alkyl Tosylates

Figure 1 (hexagons) is the linear free energy plot of positional orientation vs. base strength in eliminations from **4**. Consistent with the results for the corresponding iodide **2** (circles), the point for *tert*-butoxide (system 34) obeys the relationship, whereas that for 2,6-di-*tert*-butylphenoxide (system 39) is divergent. Vertical displacements of the points for 2,6-di-*tert*-butylphenoxide in the plots for both 2-butyl iodide and tosylate appear to be the same. Therefore, in eliminations from 2-butyl halides and arensulfonates, steric hindrance to base attack at the methylene hydrogen is independent of leaving-group identity.

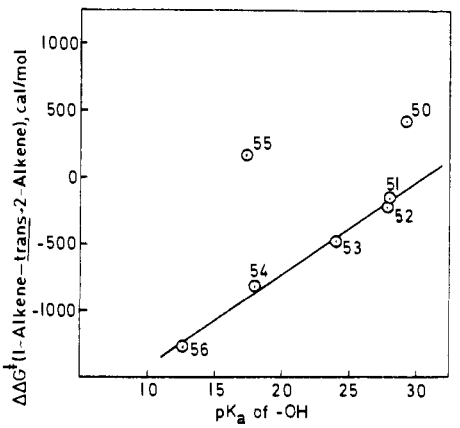


Figure 4. Plot of free-energy difference for formation of 4,4-dimethyl-1-pentene and *trans*-4,4-dimethyl-2-pentene from 4,4-dimethyl-2-pentyl tosylate vs. the pK_a of the conjugate acid of the base. System numbers refer to Table V.

The line slope for 2-butyl tosylate in Figure 1 is considerably greater than that for the corresponding iodide. This demonstrates a greater sensitivity of positional orientation to changes in base strength for the tosyloxy leaving group.

In the linear free energy plot for eliminations from **5** (Figure 3), points for both *tert*-butoxide (system 43) and 2,6-di-*tert*-butylphenoxide (system 48) fall above the line. Thus, for both 4-methyl-2-pentyl halides and arensulfonates, the degree of substrate complexity is such that *tert*-butoxide exhibits both base strength and steric effects.

Comparison of Figures 2 and 3 reveals that the vertical displacements of points for *tert*-butoxide and 2,6-di-*tert*-butylphenoxide from the lines are very similar for eliminations from **3** and **5**. From this observation and that made previously for **2** and **4**, it may be concluded that replacement of a symmetrical halogen leaving group by a dissymmetrical arenesulfonoxy leaving group does not affect the steric interactions of a bulky base. Change of leaving group should have little influence upon the base-alkyl group steric interactions indicated in **7** and **8**.

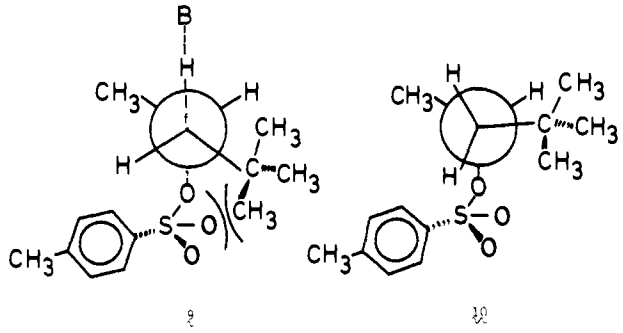
The correlation line in Figure 3 is considerably steeper than that in Figure 2. Since similar observations were made for eliminations from **2** and **4**, the greater sensitivity of positional orientation to base strength variation appears to be due to fundamental differences in transition state character for tosyloxy and iodo leaving groups.

Figure 4 presents the correlation between positional orien-

tation and base strength for eliminations from **6**. In this plot, points for *tert*-butoxide (system 50) and 2,6-di-*tert*-butylphenoxide (system 55) are displaced from the line to the same extent as was observed for **5**. This is somewhat surprising since R = *t*-Bu in **1** would be expected to provide more steric hindrance to abstraction of a methylene hydrogen than when R = *i*-Pr.

Anomalous behavior is also evident with bases for which the steric effects are absent. Thus, for eliminations from **4**, **5**, and **6** induced by *n*-propoxide, the relative percentages of *trans*-2-alkene are 30, 28, and 56, respectively. The dissimilar nature of the percentages for **5** and **6** is in sharp contrast with the orientation reported for eliminations from 4-methyl-2-pentyl and 4,4-dimethyl-2-pentyl bromides induced by NaOEt-EtOH.[19] In this work, infrared spectral analysis of the olefinic product mixtures gave the same proportion (78 ± 2%) of *trans*-2-alkene from both substrates. Therefore, the peculiar results observed for **6** may be attributed to the tosyloxy leaving group.

Examination of molecular models reveals that an anti-elimination transition state for the formation of *trans*-4,4-dimethyl-2-pentene from **6** will be destabilized by repulsions between the β *tert*-butyl group and the tosyloxy leaving groups, as depicted in **9**. The models further indicate that the preferred substrate ground state conformation **10** will deviate from a



perfectly staggered arrangement in order to relieve repulsive interactions between these two groups. The conformation **10** is very near to that required for the formation of *trans*-4,4-dimethyl-2-pentene by syn elimination. Eclipsing energy which normally reduces the propensity for syn eliminations from acyclic substrates is already present in the ground state of **6**. Hence, a syn elimination pathway for the formation of *trans*-4,4-dimethyl-2-pentene appears to be quite reasonable.

The models suggest that the anti elimination transition state for the production of 4,4-dimethyl-1-pentene from **6** remains feasible. The enhanced proportion of internal alkene relative to terminal olefin observed for eliminations from **6** (compared with **5**) may result from a better developed double bond in the syn elimination transition state.

Solvolytic Elimination

The *trans*-2-butene:*cis*-2-butene ratios observed for the solvolysis of **2** and **4** in Me_2SO (Table I, system 20, and Table III, system 42, respectively) are quite similar to those observed in the base-promoted eliminations. Such high ratios are inconsistent with the carbocation intermediate in an E1 mechanism and indicate that the mechanism may be E2 with Me_2SO acting as a weak base. Additional support for this proposal comes from the observed positional orientation for solvolytic eliminations from **2** and **4** [$\Delta\Delta G^{\ddagger}$(1-butene-*trans*-2-butene) = −1880 and −1260 cal/mol, respectively) which in Figure 1 correlates well with that expected for a very weak oxygen base (i.e., if pK_a of the conjugate acid of the base ≃ 0).

Experimental Section

Materials. Me_2SO (Fisher, reagent grade) from septum-protected bottles was used directly.[20] Conjugate acids of the bases were reagent grade (Aldrich, Fisher, Eastman) and were used without purification. *t*-BuOK (Aldrich), KH in oil (Alfa), and NaH in oil (Alfa) were used as received.

2-Butyl iodide (Eastman) was distilled under vacuum. 4-Methyl-2-pentyl iodide was prepared from 4-methyl-2-pentanol (Aldrich) using the procedure of Wiley et al.[21] as modified by Bartsch and Bunnett.[22] The compound had bp 64–65 °C (12 mm) and consistent infrared and proton magnetic resonance spectra. Anal. Calcd for $C_6H_{13}I$: C, 33.98; H, 6.13. Found (Chemalytics, Tempe, Ariz.): C, 34.25; H, 5.90. The tosylates were prepared from the corresponding alcohols (Aldrich) using Fieser's procedure.[23] Infrared and proton magnetic resonance spectra consistent with the proposed structures were obtained. **4** was an oil; **5** had mp 31–34 °C (lit.[24] mp 33–35 °C); **6** had mp 45–46 °C (lit.[25] mp 46 °C).

Base–solvent solutions were prepared by reactions of NaH or KH with the conjugate acid of the desired base in Me_2SO as previously described.[7]

Procedure. The nitrogen gas sweep procedure was the same as that previously employed.[7] Mixtures of isomeric alkenes were analyzed by flame ionization gas chromatography using the following conditions: for butenes, 40 ft × ⅛ in. column of 20% UCON-50-HB100 on Chromosorb P at room temperature or 40 ft × ⅛ in. column of 20% UCON-50-HB-280X on Chromosorb P at 0 °C; for methylpentenes, 40 ft × ⅛ in. column of 20% tricresyl phosphate on Chromosorb P at room temperature; for dimethylpentenes, 40 ft × ⅛ in. column of 20% tricresyl phosphate at 60 °C.

Control Experiments. The importance of concomitant solvolysis under the conditions of the base-promoted eliminations was assessed by allowing the substrate to react with Me_2SO in the presence of 1 equiv of 2,6-lutidine. Amounts of alkenes produced in the solvolysis were compared with the amounts of alkenes formed in reactions of the substrate with weak oxy anion bases. Synthetic mixtures of isomeric alkenes were subjected to reaction with *t*-BuOK-Me_2SO at 50 °C using the nitrogen gas sweep procedure. Alkene ratios from the samples before and after exposure to this base-solvent combination were identical, demonstrating the absence of olefinic product isomerization under the reaction conditions.

Isomerization Studies. Reaction of 4,4-dimethyl-1-pentene or *trans*-4,4-dimethyl-2-pentene with *t*-BuOK-Me_2SO at 50 °C for 30 days gave a mixture of 5.4 ± 0.5% of 4,4-dimethyl-1-pentene and 94.6 ± 0.5% of *trans*-4,4-dimethyl-2-pentene. No *cis*-4,4-dimethyl-2-pentene could be detected.

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A Study of Substituent Effects on Nitrogen Elimination from Azo Compounds via Cationic Intermediates. Acetolysis of (5-Aryl-3,5-dimethyl-1-pyrazolin-3-yl)methyl Trifluoromethanesulfonates

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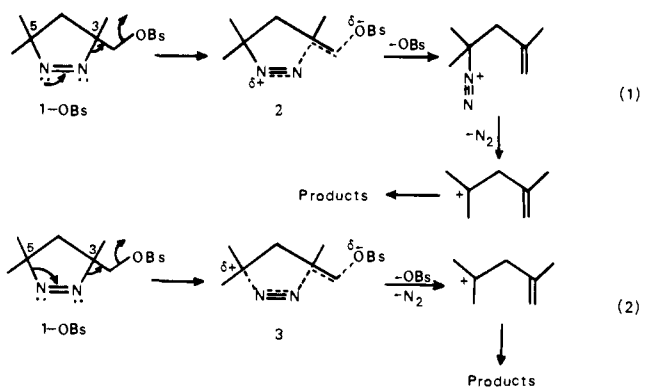
Abstract: Acetolyses of (3,5,5-trimethyl-1-pyrazolin-3-yl)methyl trifluoromethanesulfonate and a series of (5-aryl-3,5-dimethyl-1-pyrazolin-3-yl)methyl trifluoromethanesulfonates containing *p*-CH_3O, *p*-CH_3, *p*-H, and *p*-Cl substituents on the aryl ring were compared to see if the charge-stabilizing 5-aryl groups could induce a concerted one-step ionization–nitrogen elimination mechanism with C_5–N bond breaking in the rate-determining transition state. All acetolysis kinetics were strictly first order. The total reactivity spread for all of the pyrazoline trifluoromethanesulfonates was ca. 6. This compares to an expected total reactivity difference of 10^7 if appreciable C_5–N bond breaking occurs in the rate-determining step. A study with (3,5-dimethyl-5-phenyl-1-pyrazolin-3-yl)methyl and (3-methyl-5-methyl-d_3-5-phenyl-1-pyrazolin-3-yl)methyl trifluoromethanesulfonates showed a kinetic k_H/k_D value of 0.98 ± 0.01 for acetolysis. The products from acetolysis of (3,5-dimethyl-5-phenyl-1-pyrazolin-3-yl)methyl trifluoromethanesulfonate were three isomeric dienes of unrearranged carbon skeleton and a quantitative yield of nitrogen. For the 5-aryl-substituted pyrazoline trifluoromethanesulfonates, all of this is evidence that C_5–N bond breaking is not of importance in the rate-determining step. The results show that a stepwise mechanism involving C_3–N bond breaking in the rate-determining transition state to give a diazonium ion intermediate followed by formation of a 2-aryl-4-methyl-4-penten-2-yl cation is the strongly favored reaction route.

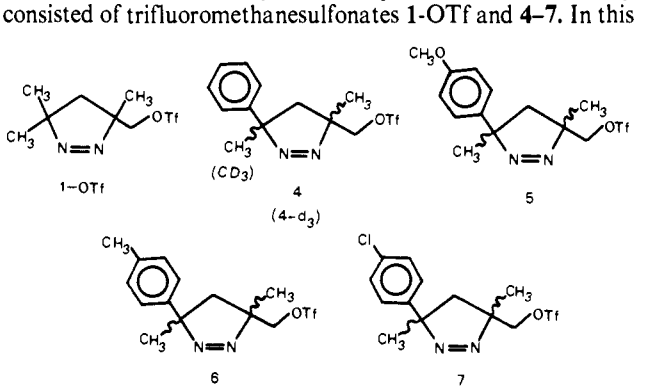
During the last 8 years investigations involving azo compound reactions have shown that the -N=N- group is one of the mechanistically most versatile functional groups in chemistry.[1-9] Examples of reactions by radical,[2,3] zwitterion,[4] carbene,[5] and cationic[6] mechanisms have been reported. Cases of concerted reaction pathways without formation of reactive intermediates[7,8] and retro-Diels–Alder processes[9] also are known.

A current research interest of ours is concerned with the mechanistic details associated with reactions of azo compounds which involve cationic intermediates.[6d] Recently we found that solvolysis of azo-*p*-bromobenzenesulfonate **1**-OBs occurs by way of a cationic mechanism which involves neighboring-group participation and extrusion of nitrogen.[6a,b] Two obvious possibilities for ionization–nitrogen elimination are shown by eq 1 and 2. A number of observations, including the nature of the products, a substantially enhanced reactivity, and a variety of different isotope effects, clearly indicate that **1**-OBs reacts via transition state **2** and eq 1.[6a] We have continued this investigation to learn more about the generality of process 1 and to see if the concerted one-step ionization–nitrogen elimination mechanism 2 can be made to occur. To evaluate these points, we have altered the structure of system **1** to include aryl groups so that the potential ability of C_5 to support positive charge can be varied in a known way. The compounds chosen for study consisted of trifluoromethanesulfonates **1**-OTf and **4–7**. In this paper we report the results of the investigation and discuss the mechanistic implications.



(1)

(2)



Results

Synthesis of the (5-Aryl-3,5-dimethyl-1-pyrazolin-3-yl)-methyl Systems. The required compounds **4–7** were prepared from the appropriate acetophenone and methyl 2-methylpro-

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