Hg free section of a vacuum line and condensed with liquid nitrogen. Propene (2 mmol) was added to the mixture and the vacuum line trap was warmed to −78° with a Dry Ice–acetone bath. The bromine disappeared at this point.

A 10-cm Vigreux column was used to remove most of the $CFCl_3$ and propene leaving a mixture of 3-bromopentane and dibromides.

Analysis of the reaction products was obtained on the tandem gas chromatograph ion chamber using column B; the results are given in the text.

threo-2,3-Dibromopentane, obtained by preparative glc separation from the above experiment, was treated with 1 equiv of *t*-BuOK in DMSO for 5 min. The volatile products were pumped into a cold trap and reanalyzed on the glc ion chamber apparatus. Two products were obtained from the dehydrohalogenation, *trans*-2-bromo-2-pentene and *trans*-3-bromo-2-pentene with equal relative molar radioactivities. Efforts to separate the dehydrohalogenation products from *erythro*-2,3-dibromopentane were unsuccessful. Authentic samples of the 2,3-dibromopentanes were made by addition of bromine to *cis*- and *trans*-2-pentenes, respectively. Dehydrohalogenations of these authentic dibromides provided samples of the bromoolefins. The 3-bromo-2-pentenes were recognized as products from dehydrohalogenation of 3,3-dibromopentane.

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Orientation in Base-Promoted β Eliminations from 2-Alkyl Halides and *p*-Toluenesulfonates. The Role of Base Association[1]

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Abstract: Base association in solvents of low polarity, such as *tert*-butyl alcohol, exerts a profound influence upon positional and geometrical orientation in base-promoted β eliminations from 2-butyl halides and *p*-toluenesulfonates. An effect of base association provides explanation for the following anomalous reports in the literature: (1) the high proportions of 1-alkene and the low *trans*-:*cis*-2-alkene ratios found in reactions of 2-alkyl halides with alkali metal alkoxides from tertiary alcohols in the corresponding alcohols or in hydrocarbon solvents; (2) the orientation dichotomy for base-promoted eliminations from 2-alkyl halides in alcoholic solvents and in dipolar aprotic solvents; and (3) the *trans*-:*cis*-2-alkene ratios of less than unity which are observed in reactions of 2-alkyl arenesulfonates with potassium hydroxide and alkoxides in *tert*-butyl alcohol. Rationalization of the effect of base association upon orientation in eliminations from 2-alkyl halides and arenesulfonates is presented.

In recent years, numerous investigations[3,6–10] have examined the effects of leaving group, base, solvent, and 2-alkyl group upon positional and geometrical orientation[11] in base-promoted β eliminations from 2-alkyl halides and arenesulfonates. We now report an unexpected effect of base association.

Eliminations from 2-Halobutanes

The experimental results in Table I provided the initial indication of the influence of base association upon orientation in base-promoted β eliminations from 2-alkyl halides and arenesulfonates. The relative amounts of olefinic products which result from reactions of 2-bromobutane with MeOK–MeOH, EtOK–EtOH, and *t*-BuOK–DMSO are insensitive to changes

Table I. Olefinic Products from Reactions of 2-Bromobutane with Potassium Alkoxides in Various Solvents at 50.0°

Base–solvent	[Base], *M*	[2-BuBr], *M*	% of 1-butene of total butenes	*trans*-2-Butene: *cis*-2-butene
MeOK–MeOH[a]	0.25	0.10	15.4[b]	3.34
MeOK–MeOH[a]	0.50	0.10	15.4	3.34
MeOK–MeOH[a]	1.00	0.10	15.4	3.41
EtOK–EtOH[a]	0.25	0.10	17.9	3.23
EtOK–EtOH[a]	0.50	0.10	17.9	3.21
EtOK–EtOH[a]	1.00	0.10	18.1	3.22
t-BuOK–*t*-BuOH[a,c]	0.10	0.10	37.7	1.86
t-BuOK–*t*-BuOH[a,c]	0.25	0.10	41.6	1.78
t-BuOK–*t*-BuOH[a,c]	0.50	0.10	44.1	1.66
t-BuOK–*t*-BuOH[a,c]	1.00	0.10	50.6	1.47
t-BuOK–*t*-BuOH[a]	1.00	0.25	49.8	1.47
t-BuOK–*t*-BuOH[a]	1.00	0.51	49.9	1.48
t-BuOK–DMSO[d]	0.10	0.09	30.5	3.04
t-BuOK–DMSO[d]	0.25	0.09	30.3	3.12
t-BuOK–DMSO[d]	0.50	0.09	30.6	3.16
t-BuOK–DMSO[d]	1.03	0.09	30.5	2.99

[a] Ampoule technique: R. A. Bartsch, *J. Org. Chem.*, **35**, 1334 (1970). [b] Maximum standard deviation from repetitive analysis, ±0.5%. [c] Reference 1. [d] Nitrogen gas sweep technique: R. A. Bartsch, *J. Org. Chem.*, **35**, 1023 (1970).

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(1) A portion of this work has appeared in preliminary form: R. A. Bartsch, G. M. Pruss, R. L. Buswell, and B. A. Bushaw, *Tetrahedron Lett.*, 2621 (1972).

(2) Department of Research Grants and Awards, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036.

(3) See ref 4 and 5 and papers cited therein.

(4) R. A. Bartsch, C. F. Kelly, and G. M. Pruss, *J. Org. Chem.*, **36**, 662 (1971).

(5) I. N. Feit and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **92**, 1630 (1970).

(6) R. A. Bartsch, *ibid.*, **95**, 3405 (1973).

(7) G. Biale, D. Cook, D. J. Lloyd, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *ibid.*, **93**, 473 (1971).

(8) I. N. Feit and L. F. Gitlin, *J. Chem Soc., Chem. Commun.*, 561 (1972).

(9) D. J. Lloyd and A. J. Parker, *Tetrahedron Lett.*, 637 (1971).

(10) N. Ono, *Bull. Chem. Soc. Jap.*, **44**, 1393 (1971).

(11) Positional orientation refers to the relative proportions of 1- and 2-alkenes which are formed, whereas geometrical orientation compares the relative amounts of *trans*-2-alkene and *cis*-2-alkene which are produced.[4]

in base concentration. In contrast, for eliminations induced by *t*-BuOK–*t*-BuOH positional and geometrical orientations are dependent upon the *t*-BuOK concentration. An increased concentration of *t*-BuOK affords a higher relative proportion of 1-butene and a lower *trans*-:*cis*-2-butene ratio.

Negligible amounts of butenes result from solvolysis of 2-bromobutane in *t*-BuOH under the conditions employed for reactions with *t*-BuOK–*t*-BuOH. Therefore, conceivable explanations for the effect of base concentration which include concomitant solvolytic and base-promoted eliminations are untenable. No change in elimination stereochemistry is involved since exclusive anti elimination has been reported for reactions of 2-bromobutane with EtOK–EtOH, *t*-BuOK–DMSO, and *t*-BuOK–*t*-BuOH.[12]

The most reasonable interpretation of these observations is an effect of base association in solvents of low polarity. In solvents of such low dielectric constant as *t*-BuOH ($\epsilon = 11.2$ at 30°),[13] *t*-BuOK undoubtedly exists to a very large extent as ion pairs and aggregates of ion pairs heavily solvated by *t*-BuOH.[14,15] However, even a small concentration of *tert*-butoxide ions could compete effectively as the elimination-inducing species because of the much greater basicity of the dissociated base in *t*-BuOH.[13] The equilibrium between dissociated and associated[16] *t*-BuOK should be concentration dependent with the proportion of associated base being enhanced by increases in the total base concentration.

We propose that the changes in orientation which attend increases in the base concentration for reactions of 2-bromobutane with *t*-BuOK–*t*-BuOH (Table I) result from a greater portion of the elimination being induced by associated *t*-BuOK when the total base concentration is increased. If this hypothesis is correct, a lower per cent of 1-butene and a higher *trans*-:*cis*-2-butene ratio should result from an increase in the proportion of dissociated base. The amount of dissociated base should be markedly enhanced by the addition of crown ethers[17,18] (macrocyclic polyethers) or dipolar aprotic compounds[19] which coordinate with potassium cations. Alternatively, changing to a tetraalkylammonium cation would greatly increase the proportion of dissociated base.[20] The results which are recorded in Table II demonstrate the anticipated decrease in the relative proportion of terminal alkene and enhancement of the *trans*-:*cis*-2-butene ratio when the dissociated base concentration is increased by addition of dicyclohexyl-18-crown-6 or the dipolar aprotic compounds hexamethylphosphortriamide, dimethylformamide, dimethyl sulfoxide, and tetramethylene sulfone to solutions of *t*-BuOK–*t*-BuOH. A more pronounced effect is noted for those dipolar aprotic compounds with a greater ability to donate electrons to cations (as indicated by higher donicity numbers). The expected changes in positional and geometrical orientation also occur when *t*-BuON-*n*-Pr$_4$ is the base.

Table II. Olefinic Products from Reaction of 2-Bromobutane[a] with 0.50 *M* *tert*-Butoxide in *t*-BuOH at 50.0°

Base	Addend	Donicity no. of addend[b]	% of 1-butene of total butenes	*trans*-2-Butene: *cis*-2-butene
t-BuOK[c,d]	None		44.1[e]	1.66
t-BuOK[d]	0.28 *M* dicyclohexyl-18-crown-6		32.5	2.92
t-BuOK[f]	0.50 *M* hexamethylphosphortriamide	38.8	36.3	2.62
t-BuOK[f]	0.50 *M* dimethylformamide	30.9	37.7	2.26
t-BuOK[f]	0.50 *M* dimethyl sulfoxide	29.8	40.5	2.42
t-BuOK[f]	0.50 *M* tetramethylene sulfone	14.8	43.4	1.92
t-BuOK[c,d,g]	None		41.6	1.78
t-BuON-*n*-Pr$_4$[c,d,g,h]	None		31.3	2.99

[a] [2-BuBr] = 0.10 *M*. [b] M. Szwarc, "Ions and Ion Pairs in Organic Reactions," M. Szwarc, Ed., Wiley-Interscience, New York, N. Y., 1972, p 5. [c] Ampoule technique, Table I, footnote *a*. [d] Reference 1. [e] Maximum standard deviation from repetitive analysis, ±0.5%. [f] Nitrogen gas sweep technique, Table I, footnote *d*. [g] [*tert*-Butoxide] = 0.25 *M*. [h] Prepared by mixing 0.25 *M* *t*-BuOK–*t*-BuOH with an appropriate amount of *n*-Pr$_4$NBr. Glpc analysis of the reaction products revealed the presence of a compound with greater volatility than butenes which was assumed to be propene produced by a competitive base-induced elimination from tetra-*n*-propylammonium ion. In view of the low basicity of tri-*n*-propylamine compared with *t*-BuOK, this side reaction should not seriously influence the butene-forming elimination.

Figures 1 and 2 illustrate the effect of varying amounts of DMSO upon positional and geometrical orientation in reactions of 2-bromobutane with 0.5 *M* *t*-BuOK–*t*-BuOH. Marked sensitivity of orientation to the amount of added DMSO is observed until a concentration of 2 to 3 *M* is reached. Further increases in the DMSO concentration produce only very small changes. These results are readily understandable if the effect of added DMSO is to increase the proportion of dissociated *t*-BuOK through solvation of potassium cations.

Nearly identical orientation is noted for eliminations from 2-bromobutane induced by *t*-BuOK–DMSO (Table I) and by *t*-BuON-*n*-Pr$_4$ or crown ether complexed *t*-BuOK in *t*-BuOH (Table II). These results establish the insensitivity of orientation to change of solvent for eliminations promoted by *dissociated* alkoxide bases. In truly concerted E2 transition states the negative charge is very diffuse so large solvation effects would not be expected.[21]

The similarity of orientation in reactions of 2-bromobutane with dissociated *tert*-butoxide in *t*-BuOH and in DMSO provides the key to understanding a dichotomy between orientation for base-induced dehy-

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(12) R. A. Bartsch, *J. Amer. Chem. Soc.*, **93**, 3683 (1971).

(13) D. Bethell and A. F. Cockerill, *J. Chem. Soc. B*, 913 (1966).

(14) D. J. Cram, C. A. Kingsbury, and B. Rickborn, *J. Amer. Chem. Soc.*, **83**, 3688 (1961).

(15) Conductivity studies of *t*-BuONa in *t*-BuOH have shown that the base exists almost entirely as ion pairs: W. H. Saunders, Jr., D. G. Bushman, and A. F. Cockerill, *ibid.*, **90**, 1775 (1968).

(16) In the absence of specific evidence regarding the actual base species present, we shall refer to contact ion pairs and aggregates of contact ion pairs as the associated species and to free ions and separated ion pairs as the dissociated base.

(17) Crown ethers strongly complex alkali metal cations: C. J. Pederson, *J. Amer. Chem. Soc.*, **89**, 7017 (1967); **92**, 391 (1970).

(18) The conductivity of *t*-BuOK in *t*-BuOH is considerably increased by addition of the crown ether dicyclohexyl-18-crown-6: M. S. Svoboda, J. Hapala, and J. Zavada, *Tetrahedron Lett.*, 265 (1972).

(19) Dipolar aprotic compounds strongly solvate potassium ions: A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

(20) Benzyltrimethylammonium *tert*-butoxide is dissociated to a much greater extent than *t*-BuOK in *t*-BuOH.[13]

(21) A. F. Cockerill, S. Rottschaefer, and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **89**, 901 (1967).

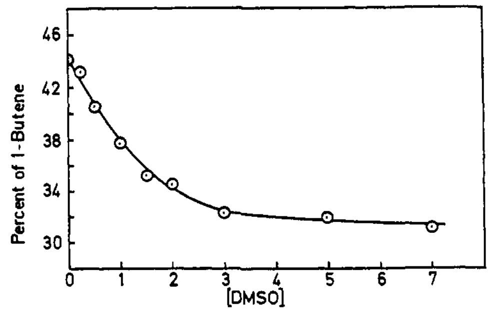


Figure 1. Per cent of 1-butene formed in reactions of 0.1 *M* 2-bromobutane with 0.5 *M* potassium *tert*-butoxide in *tert*-butyl alcohol in the presence of added dimethyl sulfoxide at 50.0°.

drohalogenations of 2-haloalkanes in alcoholic and in dipolar aprotic solvents.[4] In reactions of 2-halobutanes with a wide variety of bases in dipolar aprotic solvents, high (3.4–4.0) *trans*-:*cis*-2-butene ratios are observed which are independent of the per cent of 1-butene.[4] However, an inverse relationship between per cent of 1-butene and *trans*-:*cis*-2-butene ratio exists for reactions of 2-halobutanes with potassium alkoxides in the corresponding alcohols, as illustrated in Table III for 2-bromobutane. Eliminations from 2-bromobutane induced by primary, secondary, and tertiary alkoxides in the respective alcohols in the presence of dicyclohexyl-18-crown-6 (Table III) exhibit high *trans*-:*cis*-2-butene ratios of 2.8–3.4, which are nearly independent of the relative percentage of 1-butene. These results clearly demonstrate that the high relative proportions of 1-alkene and low *trans*-:*cis*-2-alkene ratios which result from reactions of 2-haloalkanes with metal alkoxides in alcoholic solvents of low polarity and in hydrocarbon solvents may be attributed to base association. For reactions of 2-haloalkanes with *dissociated* alkoxide bases only high *trans*-:*cis*-2-alkene ratios obtain.[6]

Table III. Olefinic Products from Reactions of 2-Bromobutane[a] with 0.25 *M* ROK in ROH at 50.0° in the Presence and Absence of 0.25 *M* Dicyclohexyl-18-crown-6

ROH of ROK–ROH	Crown ether absent[b]		Crown ether present[c]	
	% of 1-butene of total butenes	*trans*-2-Butene: *cis*-2-butene	% of 1-butene of total butenes	*trans*-2-Butene: *cis*-2-butene
Methanol	15.4[d]	3.34	16.3[d]	3.43
Ethanol	17.9	3.23	17.6	3.31
1-Propanol	19.1	3.07		
1-Hexanol	20.3	2.92		
1-Octanol	22.7	2.75		
2-Propanol	23.7	2.72	23.8	2.95
2-Butanol	25.9	2.69		
3-Pentanol	30.7	2.50		
2-Methyl-2-propanol	41.6	1.78	31.2	3.20
2-Methyl-2-butanol	48.4	1.46		
3-Methyl-3-pentanol	57.4	1.02		
3-Ethyl-3-pentanol	63.1	1.04	37.3	2.82

[a] [2-BuBr] = 0.10 *M*. [b] Ampoule technique, Table I, footnote *a*. [c] Nitrogen gas sweep technique, Table I, footnote *d*. [d] Maximum standard deviation from repetitive analysis, ±0.5%.

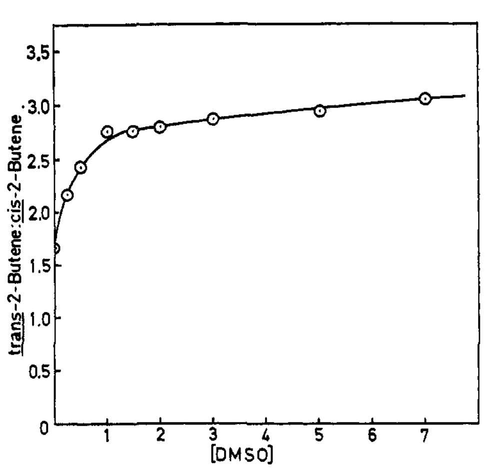
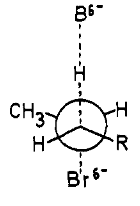


Figure 2. The *trans*-2-butene:*cis*-2-butene ratios for reactions of 0.1 *M* 2-bromobutane with 0.5 *M* potassium *tert*-butoxide in *tert*-butyl alcohol in the presence of added dimethyl sulfoxide at 50.0°.

One conceivable explanation for the observed high values of *trans*-:*cis*-2-alkene in reactions of 2-haloalkanes with dissociated bases, but low ratios for eliminations induced by associated bases, is electrostatic repulsion between the base and the leaving group. In the internal olefin-forming transition states **1** and **2**



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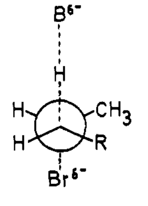

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for reactions of a 2-bromoalkane with a dissociated anionic base, there are partial negative charges on the base and the leaving group. Greater insulation of the two partial negative charges is afforded by the *trans*-alkyl groups in **1** than by the *cis*-alkyl groups in **2**. Thus, for reactions with dissociated anionic bases, **1** is favored over **2** and high *trans*-:*cis*-2-alkene ratios result. However, with associated anionic bases there is little negative charge on the base in the transition state because of interaction with the associated metal cation. Therefore, electrostatic repulsions become unimportant and *trans*-:*cis*-2-alkene ratios approaching unity are found.[22] In order to test this hypothesis, orientation in reactions of 2-halobutanes with the neutral base 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) was determined. Electrostatic repulsion between the base and leaving group is not possible for a neutral base. The high *trans*-:*cis*-2-alkene ratio of 3.6–4.6, which is observed in a variety of solvents (Table IV), clearly invalidates the electrostatic repulsion rationalization.

The dramatic differences in orientation for reactions of 2-haloalkanes with dissociated and associated alkoxide ion bases may be explained by considering the relative stabilities of the transition states leading to 1-alkene, *trans*-2-alkene, and *cis*-2-alkene (**3**, **4**, and **5**, respectively). The steric requirements of alkali metal–alkoxide ion pair aggregates should be very large. Steric interactions of an associated base with α- and

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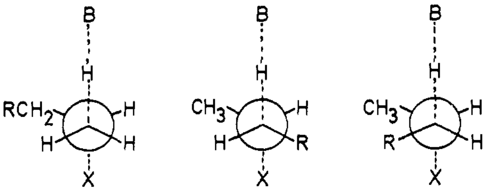
(22) We wish to thank Professor W. H. Saunders, Jr., for suggesting this interesting proposal.

Table IV. Olefinic Products from Reactions[a,b] of 2-Halobutanes with 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) in Various Solvents at 50.0°

2-BuX	Solvent	% of 1-butene of total butenes	*trans*-2-Butene: *cis*-2-butene
2-BuI	DMSO	6.5[c]	3.63
2-BuI	*t*-BuOH	5.5	4.25
2-BuI	Toluene	5.7	4.61
2-BuBr	DMSO	8.8	3.61

[a] [2-BuX] = 0.2 *M*, [DBN] = 0.5 *M*. [b] Nitrogen gas sweep technique, Table I, footnote *d*. [c] Maximum standard deviation from repetitive analysis, ±0.5%.



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β-alkyl groups should increase in the order **3** < **5** < **4**. Transition state **5** is less affected than **4** because the bulky base can be located for the most part on that side of the developing double bond where only base–hydrogen interactions occur.[23] Therefore, as a dissociated base is exchanged for an associated one, the relative proportion of 1-alkene should decrease and the *trans*-:*cis*-2-alkene ratio should increase. These predicted effects are exactly those exhibited by eliminations from 2-bromobutane which are induced by dissociated and associated alkoxide bases (Table III).

Eliminations from 2-Butyl *p*-Toluenesulfonate

In 1965, Brown and Klimisch[24] reported an intriguing predominance of *cis*-2-alkene over *trans*-2-alkene in eliminations from 2-butyl and 2-pentyl tosylates promoted by *t*-BuOK–*t*-BuOH. Necessary conditions for the preferred formation of *cis*-2-alkene appeared to be a combination of arenesulfonate as the leaving group, *t*-BuOK as the base, and *t*-BuOH as the solvent. Other workers have expanded the scope of these initial observations and have found *trans*-:*cis*-2-alkene ratios of less than unity for reactions of 2-alkyl tosylates with EtOK–*t*-BuOH,[25] KOH–*t*-BuOH,[26] and *sec*-BuOK–*sec*-BuOH.[5] In addition to arenesulfonates, other uncharged, bulky, asymmetric leaving groups, such as 2,4,6-trimethylbenzoyloxy and phenylsulfonoxy, also yield larger amounts of *cis*-2-alkene than *trans*-2-alkene in reactions of 2-substituted alkanes with *t*-BuOK–*t*-BuOH.[27] In view of the profound effect of base association upon orientation in eliminations from 2-haloalkanes, it was felt that base association might be an important factor in the unusual geometrical orientation observed for reactions of 2-alkyl tosylates with alkoxide and hydroxide ion bases in solvents of low polarity.

Relative proportions of isomeric butenes derived from reactions of 2-butyl tosylate with alkoxide ions in alcohols and in DMSO are presented in Table V. The *trans*-:*cis*-2-butene ratios are greater than one for eliminations promoted by EtOK–EtOH and *t*-BuOK–DMSO but less than unity when *t*-BuOK–*t*-BuOH is the base–solvent system. However, reaction with *t*-BuOK–*t*-BuOH in the presence of dicyclohexyl-18-crown-6 produces dramatic shifts in orientation. Geometrical orientation for the elimination promoted by *t*-BuOK–*t*-BuOH in the presence of crown ether is quite similar to that noted with EtOK–EtOH and *t*-BuOK–DMSO. This implicates dissociated alkoxide ion bases as the elimination-promoting species in all three systems, since extensive base association would not be expected in such highly polar solvents as EtOH and DMSO.

Table V. Olefinic Products from Reactions of 2-Butyl *p*-Toluenesulfonate with Various Base–Solvent Systems at 50.0°

Base	Solvent	% of 1-butene of total butenes	*trans*-2-Butene: *cis*-2-butene
EtOK[a]	EtOH	35	1.95
t-BuOK[b,c]	*t*-BuOH	63.5[d]	0.40
t-BuOK[b,e,f]	*t*-BuOH	53.6[d]	1.88
t-BuOK[b,f]	DMSO	57.3[d]	2.21

[a] At 55°: D. H. Froemsdorf and M. E. McCain, *J. Amer. Chem. Soc.*, **87**, 3984 (1965). [b] Reference 1, [*tert*-BuOK] = 0.5 *M*, [2-BuOTs] = 0.1 *M*. [c] Ampoule technique, Table I, footnote *a*. [d] Maximum standard deviation from repetitive analysis, ±0.5%. [e] Dicyclohexyl-18-crown-6 (0.29 *M*) present. [f] Nitrogen gas sweep technique, Table I, footnote *d*.

Preferential formation of *cis*-2-butene over *trans*-2-butene in reactions of 2-butyl tosylate with *t*-BuOK–*t*-BuOH may be readily rationalized by modification of Brown's steric model[24] to account for the large steric requirements of an associated base.

Experimental Section

Materials. The 2-halobutanes were purified commercial products. 2-Butyl tosylate was prepared from 2-butanol by standard procedures. Dicyclohexyl-18-crown-6[28] (Aldrich), 1,5-diazabicyclo-[4.3.0]non-5-ene (Aldrich), potassium *tert*-butoxide (MSA),[29] hexamethylphosphortriamide (Aldrich), tetramethylene sulfone (Aldrich), and anhydrous ethanol were used directly. Dimethyl sulfoxide and dimethylformamide (Baker, reagent) were stored over molecular sieves. Methanol was purified by reaction with magnesium.[30] All other alcohols, except ethanol, were purified by distillation from calcium hydride.

Base–Solvent Solutions. Solutions of potassium alkoxides in the corresponding alcohols were prepared by reaction of clean, freshly cut potassium metal with the alcohols under dry nitrogen.[31] Solutions of dipolar aprotic compounds and *t*-BuOK in *t*-BuOH resulted from adding weighed amounts of the dipolar aprotic compounds to *t*-BuOK–*t*-BuOH solutions. Solutions of *t*-BuOK–DMSO were prepared immediately before use by dissolving weighed amounts of *t*-BuOK in DMSO.

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(23) The principal features of this explanation have been previously advanced: H. C. Brown and R. L. Klimisch, *J. Amer. Chem. Soc.*, **88**, 1425 (1966). An important difference between our proposal and Brown's is the point at which steric effects become important. Steric interactions are significant only with very large dissociated bases[6] and with associated bases.

(24) H. C. Brown and R. L. Klimisch, *ibid.*, **87**, 5517 (1965).

(25) D. H. Froemsdorf, W. Dowd, and K. E. Leimer, *ibid.*, **88**, 2345 (1966).

(26) D. H. Froemsdorf and M. D. Robins, *ibid.*, **89**, 1737 (1967).

(27) R. A. Bartsch and J. F. Bunnett, *ibid.*, **91**, 1376 (1969).

(28) A mixture of two isomers: H. K. Frensdorf, *ibid.*, **93**, 4684 (1971).

(29) We wish to thank MSA Research Corporation, Evans City, Pa., for a generous sample of this compound.

(30) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath, Boston, Mass., 1957, p 289.

(31) D. S. Bailey and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **92**, 6904 (1970).

Reactions Procedures. Reactions of 2-butyl halides and tosylate with the various base–solvent solutions were carried out using either an ampoule technique[32] or a nitrogen gas sweep method[33] (10-min reaction time) as indicated in the tables. Elimination products were analyzed by glpc as before.[32,33]

Control Experiments. Negligible amounts of butenes resulted from the solvolysis of 2-butyl bromide and tosylate in *tert*-BuOH at 50° in the presence of 2,6-lutidine[34] for reaction periods comparable with those employed in reactions with *t*-BuOK–*t*-BuOH. Formation of butenes by solvolysis of 2-butyl bromide and iodide in various other solvents was shown to be insignificant when compared with the corresponding base-promoted reactions.

Acknowledgment. A portion of this research was supported by a Grant-in-Aid of Research from the Society of the Sigma Xi.

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[32] R. A. Bartsch, *J. Org. Chem.*, **35**, 1334 (1970).

[33] R. A. Bartsch, *ibid.*, **35**, 1023 (1970).

[34] Present to prevent acid-catalyzed reactions of substrate or products.

Electrophilic Additions to Dienes. III.[1,2]
Hydrochlorination of Phenylallene and Its Derivatives

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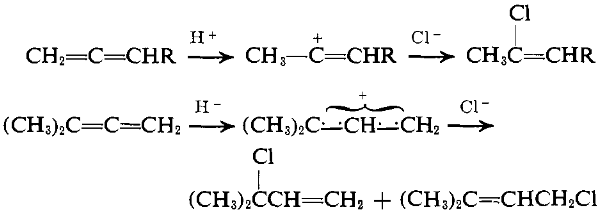
Abstract: The hydrochlorination of phenylallene and its derivatives (p-CH$_3$, m-CH$_3$, p-Cl, m-Cl, α-CH$_3$, and γ-CH$_3$) has been investigated in glacial acetic acid. The product of each reaction was exclusively cinnamyl chloride or its derivative. The kinetic order of the reaction with respect to hydrogen chloride was one at lower concentrations ([HCl] = 0.10–0.25 *M*) and two at higher concentrations ([HCl] = 0.64–1.33 *M*). The effects of ring substituents on the reaction rate obey the Hammett-type relationship with Brown–Okamoto's σ^+ giving $\rho^+ = -4.20$ ([HCl] = 0.955 *M*, 30.4°). The α- and γ-methyl substitutions accelerate the reaction by a factor of 4000 and 200, respectively. These results led us to conclude that the hydrochlorination of phenylallene proceeds through a transition state which structurally resembles the perpendicularly twisted α-vinylbenzyl cation.

Although the electrophilic addition reactions to allenic compounds have been studied fairly widely,[3] factors which determine the course of reaction are not at all understood. The investigations so far available are concerned only with the orientation[4] and the stereochemistry[5] of addition. Surprisingly, no information is available with regard to the kinetic phase of the reaction.[6]

The orientation of addition depends both on the structure of allene and on the nature of electrophile. In the case of hydrochlorination, a proton, the simplest electrophile, attacks the terminal methylene of allene and monoalkylallenes to give vinylic cation while it attacks the central carbon of 1,1-dimethylallene leading to allylic cation.[3,4a] Because of the conjugative nature of an intermediate allylic cation, the product studies of the latter type of reaction cannot establish which double bond is attacked first by the proton.



$$\mathrm{CH_2{=}C{=}CHR} \xrightarrow{\mathrm{H^+}} \mathrm{CH_3{-}\overset{+}{C}{=}CHR} \xrightarrow{\mathrm{Cl^-}} \mathrm{CH_3\overset{\overset{\displaystyle Cl}{|}}{C}{=}CHR} \quad (1)$$

$$\mathrm{(CH_3)_2C{=}C{=}CH_2} \xrightarrow{\mathrm{H^-}} \mathrm{(CH_3)_2C\overbrace{\cdots CH \cdots}^{+}CH_2} \xrightarrow{\mathrm{Cl^-}} \mathrm{(CH_3)_2\overset{\overset{\displaystyle Cl}{|}}{C}CH{=}CH_2 + (CH_3)_2C{=}CHCH_2Cl} \quad (2)$$

The present paper reports the results of kinetic studies on the hydrochlorination of phenylallene and its derivatives and establishes the orientation of addition in the rate-determining step. Furthermore, the nature of the transition state in the protonation of phenylallene will be clarified.

Results

Product Analysis. Hydrochlorination of phenylallene **1** was undertaken in glacial acetic acid at [HCl] = 0.955 *M*. The reaction proceeds at a moderate rate at room temperature. The reaction for 2 days gave exclusively cinnamyl chloride (>99% by nmr; isolated in 95% yield). The product isolated by distillation was compared with an authentic sample. No sign of the formation of the isomeric chlorides was observed. Careful examination of the product revealed formation of a small amount of an acetate (<0.5% by nmr).

Kinetic Studies. Initial rates *R* for the reaction were gas chromatographically measured as a function of the concentrations of **1** and HCl. Logarithmic plots of *R vs.* [HCl] at [**1**] = 0.455 *M* are shown in Figure 1. The slope was calculated by the method of least squares to be 1.97. Similar plots of *R vs.* [**1**] at [HCl] = 0.955

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[2] Part II: T. Okuyama, T. Sakagami, and T. Fueno, *Tetrahedron*, **29**, 1503 (1973).

[3] For reviews, see K. Griesbaum, *Angew. Chem., Int. Ed. Engl.*, **5**, 933 (1966); D. R. Taylor, *Chem. Rev.*, **67**, 317 (1967).

[4] (a) T. L. Jacobs and R. N. Johnson, *J. Amer. Chem. Soc.*, **82**, 6397 (1960); (b) H. G. Peer, *Recl. Trav. Chim. Pays-Bas*, **81**, 113 (1962); (c) W. L. Waters and E. F. Kiefer, *J. Amer. Chem. Soc.*, **89**, 6261 (1967); (d) T. L. Jacobs and R. Macomber, *J. Org. Chem.*, **33**, 2988 (1968).

[5] (a) T. L. Jacobs, R. Macomber, and D. Zunker, *J. Amer. Chem. Soc.*, **89**, 7001 (1967); (b) W. L. Waters, W. S. Linn, and M. C. Caserio, *ibid.*, **90**, 6741 (1968); (c) R. D. Bach, *ibid.*, **91**, 1771 (1969); (d) M. C. Findlay, W. L. Waters, and M. C. Caserio, *J. Org. Chem.*, **36**, 275 (1971).

[6] The kinetic discussion is reported only in ref 4a. Unfortunately, the investigation without solvent and at low temperature made it qualitative.

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