Orientation in Base-Promoted 1,2-Elimination Reactions. Nitrogen and Carbon Bases [1]

Richard A. Bartsch,* Debra K. Roberts,[2] and Bong Rae Cho[2]

Department of Chemistry, Texas Tech University, Lubbock, Texas 79409

Received June 16, 1979

Orientation in 1,2-eliminations from 2-iodobutane promoted by a variety of nitrogen and carbon bases in dimethyl sulfoxide has been determined. By variation of the base counterion from sodium to potassium then potassium in the presence of 18-crown-6, the importance of ion pairing for nitrogen and carbon bases was explored. Using linear free energy relationships, we demonstrated that sensitivity of positional orientation to base strength variation is the same for amide ion and oxyanion bases. However, for methide ion bases, the sensitivity of positional orientation to base strength change was very dependent upon the base type.

Fundamental control of positional orientation by base strength has been demonstrated in oxyanion-promoted olefin formation from 2-alkyl halides and tosylates.[3,4] Linear free energy relationships were observed when the difference in transition state free energies for formation of positional isomers[5] was plotted against the oxyanion base strength. Divergence of points from such correlations was attributed to the onset of base steric interactions.[3,4]

In order to suppress complicating association of oxyanion bases with alkali metal cations,[6] these reactions were conducted in dimethyl sulfoxide (Me_2SO). Insensitivity of orientation to variation of the cation was used to demonstrate that dissociated oxyanion bases were the effective base species.[4] Thus, reactions of 2-iodobutane with *tert*-butoxide ion in Me_2SO gave the same elimination orientation when the cation was sodium, potassium, or potassium complexed with the crown ether 18-crown-6.[4]

In an earlier study,[7] it was assumed that the high cation solvating ability of Me_2SO would also be sufficient to provide dissociated amide and methide ion bases. For that study, bases were generated by the reaction of sodium hydride with the conjugate acid of the base. Potassium hydride was not commercially available at that time. Recently, we and others[8] have discovered that orientation in eliminations from 2-iodobutane induced by potassium dimsyl in Me_2SO is significantly different from that reported previously for sodium dimsyl.[7] In order to probe the importance of the indicated base ion pairing, we determined the effect of base cation variation upon orientation in eliminations from 2-iodobutane induced by a variety of methide and amide ion bases. The influence of base strength in controlling orientation for carbon and nitrogen bases could be determined under conditions where complicating base ion pairing was absent by use of this information. Results of this investigation are now reported.

Results

Reactions of 2-iodobutane with methide and amide ion bases in Me_2SO were conducted at 50 °C, utilizing a nitrogen gas sweep procedure which prevents isomerization of the isomeric products by the strongly basic medium.[4,7] Appropriate control experiments demonstrated that negligible amounts of butenes were produced by solvolysis of 2-iodobutane under the conditions employed for the base-promoted eliminations.

Table I. Relative Olefinic Products[a] from Reactions of 2-Iodobutane with Dimsyl Ion in Me_2SO at 50.0 °C

system	cation of the base	% of total butenes: 1-butene	% of total butenes: *trans*-2-butene	% of total butenes: *cis*-2-butene	*trans*-2-butene: *cis*-2-butene
1	K^+ + 18C6[b]	20.5	60.9	18.6	3.3
2	K^+	19.7	61.0	19.3	3.2
3	Na^+ + 18C6	16.1	64.4	19.5	3.3
4	Na^+	9.5	68.6	21.9	3.1

[a] Relative alkene proportions are reproducible to ±0.5%. [b] 18-Crown-6.

The relative proportions of 1-butene, *trans*-2-butene, and *cis*-2-butene formed in reactions of 2-iodobutane with dimsyl ion in Me_2SO are recorded in Table I. Positional orientation[5] is clearly influenced by the identity of the cation. The relative percentages of 1-butene increase with cation variation $Na^+ < Na^+ + \text{18-crown-6} < K^+ < K^+ + \text{18-crown-6}$. In contrast, the *trans*-2-butene:*cis*-2-butene ratios are apparently insensitive to cation variation.

In order to determine the influence of the first atom of the base (nitrogen or carbon) and the basicity of the base upon such ion pairing effects, orientation was measured for eliminations from 2-iodobutane induced by a variety of amide and methide ion bases. Results obtained with conjugate bases derived from anilines, amides and sulfonamides, sulfones, ketones, and toluenes are presented in Tables II–VI, respectively.

Plots of free energy differences between transition states for formation of 1-butene and *trans*-2-butene, $\Delta\Delta G^{\ddagger}$ (1-butene − *trans*-2-butene), vs. pK_a values in Me_2SO for the conjugate acids of the nitrogen and carbon bases are shown in Figure 1–4.

Discussion

Base-promoted eliminations from alkyl halides are among the least controversial examples of the concerted E2 mechanism.[4] Low acidity of β hydrogens in such compounds renders carbanionic mechanisms highly unlikely. Since control experiments demonstrated a negligible contribution of solvolytic elimination under the conditions employed for the base-promoted reactions, it seems most reasonable that the reactions of 2-iodobutane with anionic nitrogen and carbon bases in Me_2SO proceed via the E2 mechanism.

Effects of Base Ion Pairing upon Orientation. The influence of base ion pairing upon orientation in eliminations from 2-iodobutane induced by dimsyl ion in Me_2SO is shown by the data in Table I. The relative percentage

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[1] This research was supported by the Robert A. Welch Foundation, Grant D-638.

[2] Predoctoral Fellow of the Robert A. Welch Foundation.

[3] R. A. Bartsch, G. M. Pruss, B. A. Bushaw, and K. E. Weigers, *J. Am. Chem. Soc.*, **95**, 3405 (1973).

[4] R. A. Bartsch, R. A. Read, D. T. Larsen, D. K. Roberts, K. J. Scott, and B. R. Cho, *J. Am. Chem. Soc.*, **101**, 1176 (1979).

[5] Positional orientation refers to the relative amounts of 1-alkene and 2-alkenes which are formed. Geometrical orientation compares the relative amounts of *trans*-2-alkene and *cis*-2-alkene.

[6] R. A. Bartsch, *Acc. Chem. Res.*, **8**, 239 (1975).

[7] R. A. Bartsch, K. E. Wiegers, and D. M. Guritz, *J. Am. Chem. Soc.*, **96**, 430 (1974).

[8] B. J. Kane, G. Marcelin, and S. N. Traynor, unpublished results.

0022-3263/79/1944-4105$01.00/0

Table II. Relative Olefinic Products[a] from Reactions of 2-Iodobutane with Anilide Bases in Me_2SO at 50.0 °C

system	conjugate acid of base	pK_a of conjugate acid of base	cation of base	% of total butenes		
				1-butene	*trans*-2-butene	*cis*-2-butene
5	*m*-methylaniline	31.0[b]	K^+ + 18C6[c]	17.1	63.6	19.3
6	*m*-methylaniline		K^+	15.9	64.3	19.8
7	aniline	30.7[b]	K^+ + 18C6	16.8	64.0	19.2
8	aniline		K^+	14.6	66.3	19.1
9	*m*-chloroaniline	28.5[b]	K^+ + 18C6	16.3	64.3	19.4
10	*m*-chloroaniline		K^+	12.8	66.5	20.7
11[d]	*m*-chloroaniline		Na^+	11.8	68.7	19.5
12	*p*-cyanoaniline	25.3[b]	K^+ + 18C6	11.2	69.1	19.7
13	*p*-cyanoaniline		K^+	11.1	69.6	19.3
14[d]	*p*-cyanoaniline		Na^+	9.8	70.0	20.2
15	2,5-dichloroaniline	24.6[e]	K^+ + 18C6	11.2	68.1	20.7
16	2,5-dichloroaniline		K^+	11.2	68.0	20.8
17[d]	2,5-dichloroaniline		Na^+	9.6	71.1	19.3
18	*p*-nitroaniline	20.9[b]	K^+ + 18C6	8.3	70.9	20.8
19	*p*-nitroaniline		K^+	8.0	71.0	21.0
20	4-chloro-2-nitroaniline	18.9[f]	K^+ + 18C6	7.8	68.5	23.7
21	4-chloro-2-nitroaniline		K^+	7.4	69.6	23.0
22[d]	4-chloro-2-nitroaniline		Na^+	7.2	71.6	21.2

[a] Relative alkene proportions are reproducible to ±0.5%. [b] F. G. Bordwell, D. Algrim, and N. R. Vanier, *J. Org. Chem.*, 42, 1817 (1977). [c] 18-Crown-6. [d] Reference 7. [e] J. Courtot-Coupez and M. LeDemezet, *Bull. Soc. Chim. Fr.*, 1033 (1969). [f] W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, G. E. Drucker, Z. Margolin, R. J. McCallum, G. J. McCollum, and N. R. Vanier, *J. Am. Chem. Soc.*, 97, 7006 (1975).

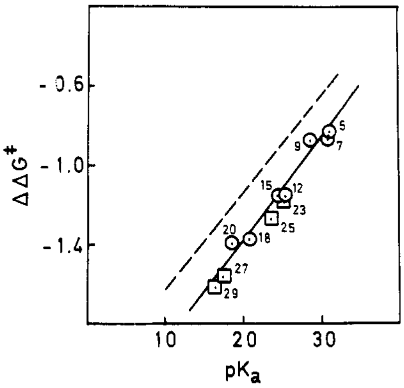


Figure 1. Plot of the free energy differences for formation of 1-butene and *trans*-2-butene in kcal/mol vs. the pK_a of the conjugate acids of anilide bases (circles) and bases derived from amides and sulfonamides (squares). System numbers refer to Tables II and III. The dashed line is that reported for oxyanion bases.

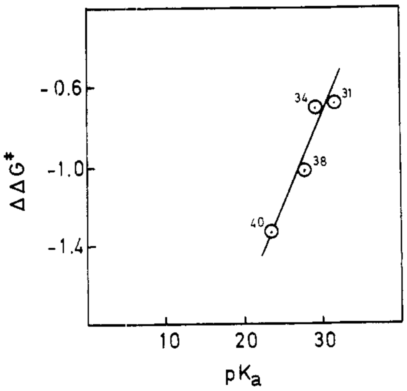


Figure 2. Plot of the free energy difference for formation of 1-butene and *trans*-2-butene in kcal/mol vs. the pK_a of the conjugate acids of bases derived from sulfones. System numbers refer to Table IV.

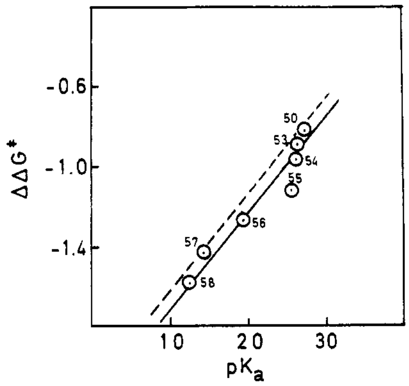


Figure 3. Plot of the free energy difference for formation of 1-butene and *trans*-2-butene in kcal/mol vs. the pK_a of the conjugate acids of enolate bases. System numbers refer to Table V.

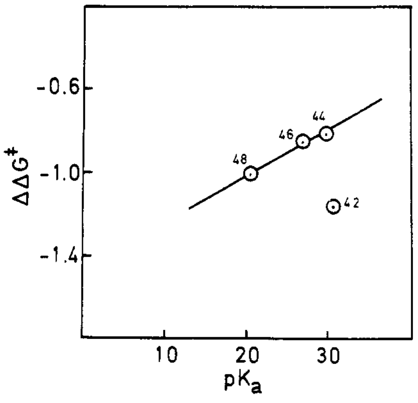


Figure 4. Plot of the free energy difference for formation of 1-butene and *trans*-2-butene in kcal/mol vs. the pK_a of the conjugate acids of toluide bases. System numbers refer to Table VI.

of 1-butene increases substantially when the dimsyl counterion is changed from sodium (system 4) to potassium (system 2). This cation variation should markedly reduce the degree of cation–dimsyl ion interaction. Addition of the strong alkali metal cation complexing agent 18-crown-6 produces a significant enhancement of the relative proportion of 1-butene observed for sodium dimsyl (compare systems 3 and 4) but not for potassium dimsyl (compare systems 1 and 2). These results indicate that an ion-paired base is the effective base species for the former, but for the latter it is the free dimsyl anion. For sodium dimsyl, even the presence of 18-crown-6 is insufficient to produce the orientation characteristic of the free dimsyl anion.

Table III. Relative Olefinic Products[a] from Reactions of 2-Iodobutane with Anionic Bases Derived from Amides and Sulfonamides in Me_2SO at 50.0 °C

				% of total butenes		
system	conjugate acid of base	pK_a of conjugate acid of base	cation of base	1-butene	*trans*-2-butene	*cis*-2-butene
23	acetamide	25.5[b]	K^+ + 18C6[c]	10.7	68.1	21.2
24	acetamide		K^+	11.0	66.5	22.5
25	benzamide	23.35[b]	K^+ + 18C6	9.6	70.1	20.3
26	benzamide		K^+	10.0	68.5	21.5
27	methanesulfonamide	17.5[b]	K^+ + 18C6	6.2	73.2	20.6
28	methanesulfonamide		K^+	6.7	71.0	22.3
29	benzenesulfonamide	16.1[d]	K^+ + 18C6	5.9	73.5	20.6
30	benzenesulfonamide		K^+	5.9	73.7	20.4

[a] Relative alkene proportions are reproducible to ±0.5%. [b] F. G. Bordwell and D. Algrim, *J. Org. Chem.*, 41, 2507 (1976). [c] 18-Crown-6. [d] F. G. Bordwell, private communication.

Table IV. Relative Olefinic Products[a] from Reactions of 2-Iodobutane with Anionic Bases Derived from Sulfones in Me_2SO at 50.0 °C

				% of total butenes		
system	conjugate acid of base	pK_a of conjugate acid of base	cation of base	1-butene	*trans*-2-butene	*cis*-2-butene
31	$CH_3SO_2CH_3$	31.1[b]	K^+ + 18C6[c]	20.9	59.5	19.6
32	$CH_3SO_2CH_3$		K^+	17.9	61.3	20.8
33[d]	$CH_3SO_2CH_3$		Na^+	8.9	68.5	22.6
34	$C_6H_5SO_2CH_3$	29.0[b]	K^+ + 18C6	20.5	60.5	19.0
35	$C_6H_5SO_2CH_3$		K^+	21.0	59.5	19.5
36	$C_6H_5SO_2CH_3$		Na^+ + 18C6	19.6	58.7	21.7
37	$C_6H_5SO_2CH_3$		Na^+	9.6	67.4	23.0
38	$C_6H_5SO_2CH_2OC_6H_5$	27.9[e]	K^+ + 18C6	13.3	65.8	20.9
39	$C_6H_5SO_2CH_2OC_6H_5$		K^+	13.5	66.1	20.4
40	$C_6H_5SO_2CH_2SCH_3$	23.4[e]	K^+ + 18C6	8.8	69.9	21.3
41	$C_6H_5SO_2CH_2SCH_3$		K^+	8.3	70.4	21.3

[a] Relative alkene proportions are reproducible to ±0.5%. [b] W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, G. E. Drucker, Z. Margolin, R. J. McCallum, G. J. McCollum, and N. R. Vanier, *J. Am. Chem. Soc.*, 97, 7006 (1975). [c] 18-Crown-6. [d] Reference 7. [e] F. G. Bordwell, D. Algrim, and N. R. Vanier, *J. Org. Chem.*, 42, 1817 (1977).

Table V. Relative Olefinic Products[a] from Reactions of 2-Iodobutane with Enolate Bases in Me_2SO at 50.0 °C

				% of total butenes		
system	conjugate acid of base	pK_a of conjugate acid of base	cation of base	1-butene	*trans*-2-butene	*cis*-2-butene
42	$CH_3CH_2C(O)CH_2CH_3$	27.1[b]	K^+ + 18C6[c]	17.4	62.4	20.2
43	$CH_3CH_2C(O)CH_2CH_3$		K^+	16.6	62.4	21.0
44	$CH_3CH_2C(O)CH_2CH_3$		Na^+	16.5	63.6	19.9
45	$CH_3C(O)CH_3$	26.5[b]	Na^+	16.0	64.1	19.9
46	$C_6H_5C(O)CH(CH_3)_2$	26.3[b]	Na^+	14.4	64.8	20.8
47	$C_6H_5C(O)CH_3$	24.7[b]	Na^+	12.2	69.2	18.6
48	$C_6H_5CH_2C(O)CH_3$	19.4[d]	Na^+	9.8	70.8	19.4
49	$CH_3C(O)CH_2C(O)CH_3$	13.4[d]	Na^+	7.6	71.1	21.3
50	$C_6H_5C(O)CH_2C(O)CH_3$	12.7[d]	Na^+	6.3	74.5	19.2

[a] Relative alkene proportions are reproducible to ±0.5%. [b] W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, G. E. Drucker, Z. Margolin, R. J. McCallum, G. J. McCollum, and N. R. Vanier, *J. Am. Chem. Soc.*, 97, 7006 (1975). [c] 18-Crown-6. [d] F. G. Bordwell, J. E. Bartmess, G. E. Drucker, Z. Margolin, and W. S. Matthews, *J. Am. Chem. Soc.*, 97, 3226 (1975). [e] Reference 7.

Table VI. Relative Olefinic Products[a] from Reactions of 2-Iodobutane with Toluide Bases in Me_2SO at 50.0 °C

				% of total butenes		
system	conjugate and of base	pK_a of conjugate acid of base	cation of base	1-butene	*trans*-2-butene	*cis*-2-butene
51	*p*-$NCC_6H_4CH_3$	30.8[b]	K^+ + 18C6[c]	11.3	69.2	19.5
52	*p*-$NCC_6H_4CH_3$		K^+	11.1	69.6	19.3
53	*p*-$C_6H_5SO_2C_6H_4CH_3$	29.8[b]	K^+ + 18C6	17.8	63.5	18.7
54	*p*-$C_6H_5SO_2C_6H_4CH_3$		K^+	17.5	63.6	18.9
55	*p*-$C_6H_5C(O)C_6H_4CH_3$	26.9[b]	K^+ + 18C6	17.1	63.6	19.3
56	*p*-$C_6H_5C(O)C_6H_4CH_3$		K^+	17.6	63.0	19.4
57	*p*-$NO_2C_6H_4CH_3$	20.4[b]	K^+ + 18C6	13.4	64.5	22.1
58	*p*-$NO_2C_6H_4CH_3$		K^+	13.6	63.9	22.5

[a] Relative alkene proportions are reproducible to ±0.5%. [b] F. G. Bordwell, D. Algrim, and N. R. Vanier, *J. Org. Chem.*, 42, 1817 (1977). [c] 18-Crown-6.

Although base ion pairing affects positional orientation, geometrical orientation[5] is insensitive to cation variation or the presence of 18-crown-6 (Table I). In previous studies of eliminations from 2-iodobutane induced by oxyanion bases in Me_2SO, it was noted that a change to a weaker base decreased the relative proportion of 1-butene but gave an invarient *trans*-2-butene:*cis*-2-butene ratio.[3,4] Therefore, the present findings suggest that base ion pairing in Me_2SO influences positional orientation by producing a weaker base species.

These results are in sharp contrast with the influence of cation–base interactions upon orientation in solvents of low polarity.[6] For example, reaction of 2-bromobutane with 1.0 M *t*-BuOK in *t*-BuOH at 50 °C yields 51% of 1-butene, and *trans*-2-butene:*cis*-2-butene = 1.5. In the presence of 1 equiv of dicyclohexano-18-crown-6, the elimination produces 31% of 1-butene, and *trans*-2-butene:*cis*-2-butene = 3.2 (olefinic proportions which are essentially identical with those formed when the base–solvent system is *t*-BuOK in Me_2SO).[9] Thus, in *t*-BuOH, base ion pairing causes an increase in the relative percentage of 1-butene and a much lower *trans*-2-butene:cis-2-butene ratio. The divergent effects of base ion pairing in Me_2SO and in *t*-BuOH may be readily rationalized if monomeric ion pairs are the effective base species in Me_2SO, but in *t*-BuOH the active base is an aggregate of ion pairs which is not only a weaker base species but also has large steric requirements.[6,9]

Nitrogen Bases. Orientation for eliminations from 2-iodobutane promoted by anilide bases in Me_2SO is recorded in Table II. The range of anilide base strengths covers 12 pK units.

The orientation data in Table II demonstrate that base ion pairing in Me_2SO becomes important with the stronger anilide bases. Thus, cation variation from Na^+ to K^+ to K^+ + 18-crown-6 produces no perceptible orientation change when the base is 4-chloro-2-nitroanilide (pK = 18.9) (systems 20–22). However, the same cation variation yields a small, but significant, change in positional orientation for *m*-chloroanilide (pK = 28.5) (systems 9–11). Although orientation changes observed for cation variation of bases with pK values near 25 (systems 12–17) are suggestive of some base ion pairing for the sodium anilides, differences in relative alkene proportions are barely outside of experimental error.

For the series of anilide bases, comparison of orientation obtained for the potassium anilide in the absence and presence of 18-crown-6 reveals no significant differences even with the strongest anilide base (compare systems 5 and 6). As previously noted for free oxyanion bases,[3,4] increasing base strength of the free anilide bases enhances the relative proportion of terminal alkene but has no apparent influence upon geometrical orientation.

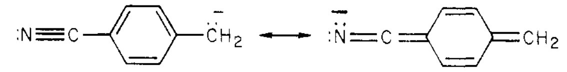
Figure 1 shows a linear free energy relationship between positional orientation and anilide base strength (circles) when orientation data for potassium anilide bases in the presence of 18-crown-6 are used. Comparison of the slope of the line prescribed by anilide bases (circles) with the dashed line for oxyanion bases[4] in Figure 1 reveals a very similar influence of changes in base strength upon orientation for the nitrogen and oxygen bases. However, oxyanions uniformly yield a slightly higher percentage of 1-butene (2–4%) than anilide bases of comparable strength.

Orientation for reactions of 2-iodobutane with anionic bases derived from amides and sulfonamides in Me_2SO is presented in Table III. In Figure 1, an excellent correlation of positional orientation noted for these bases (squares) with that observed for the anilide bases (circles) is evident.

Carbon Bases. Reactions of 2-iodobutane with anionic bases obtained from several sulfones in Me_2SO produce the orientation data listed in Table IV. Effects of cation variation upon orientation in reactions involving the anions of dimethyl sulfone and methyl phenyl sulfone demonstrate the importance of base ion pairing when the cation is sodium. Positional orientation obtained using potassium counterions in the presence of 18-crown-6 yields the linear free energy relationship shown in Figure 2. The line slope in Figure 2 is considerably steeper than that of either the solid or dashed lines in Figure 1. Thus, positional orientation in eliminations induced by these carbon bases is considerably more sensitive to base strength variation that is that observed with oxygen and nitrogen bases.

Orientation for reactions of 2-iodobutane with enolate anions in Me_2SO is presented in Table V. The unimportance of base ion pairing for even the strongest enolate ion base examined is demonstrated by the insensitivity of positional orientation to cation variation (compare systems 42, 43, and 44). Therefore, older data obtained with sodium enolates may be used for the linear free energy relationship between positional orientation and enolate ion base strength shown in Figure 3. The prescribed line is closely positioned and precisely parallel to the dashed line for oxyanion bases. When this correspondence is combined with the evidence for the absence of ion pairing with enolate bases, proton abstraction by enolate oxygen, rather than carbon, is strongly indicated.

The final carbon base system examined involves eliminations from 2-iodobutane promoted by toluide bases in Me_2SO (Table VI). Positional orientation is compared with toluide base strength in Figure 4. Three of the points fall on a line with the fourth divergent. Lack of correlation for the *p*-cyanobenzyl anion point suggests that the base may attack through the nitrogen of resonance form **2**



1 **2**

rather than the carbon of **1**.

The slope of the correlation line in Figure 4 is much less than that observed for sulfone-derived carbon bases. Thus, the sensitivity of positional orientation to changes in carbon base strength is found to be highly dependent upon the nature of the methide ion base. This difference may be due to differing degrees of negative charge dispersal in the carbanionic bases. Negative charge on the benzylic carbon of a toluide ion base should be highly dispersed by resonance, whereas carbanions α to a sulfonyl group are thought to be localized.[10]

Experimental Section

Materials. Me_2SO (Fisher, reagent grade) from septum-protected bottles was used directly. Conjugate acids of the bases were reagent grade (Aldrich, Fisher, Eastman) and were used without purification. NaH in oil (Alfa), KH in oil (Alfa), and 18-crown-6 (Aldrich) were used as received. 2-Iodobutane (Eastman) was distilled under vacuum and stored in a brown bottle in a refrigerator.

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

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(9) R. A. Bartsch, G. M. Pruss, D. M. Cook, R. L. Buswell, B. A. Bushaw, and K. E. Wiegers, *J. Am. Chem. Soc.*, **95**, 6745 (1973).

(10) H. E. Zimmerman and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **82**, 2505 (1960).

Procedure. The nitrogen gas sweep procedure was the same as that previously employed.[7] In the reaction solutions, [2-BuI] = 0.1 M and [base] = 0.25 M. In some reactions, 0.25 M 18-crown-6 was present. Trapped butene products were analyzed by gas chromatography.[4]

Control Experiment. The importance of concomitant solvolysis under the conditions of the base-promoted eliminations was assessed by allowing 2-iodobutane to react with Me_2SO at 50.0 °C in the presence of 1 equiv of 2,6-lutidine. The amount of butenes formed by solvolysis was much less than that produced by reaction of 2-iodobutane with the weakest bases examined.

Registry No. 2-Iodobutane, 513-48-4; 1-butene, 106-98-9; *trans*-2-butene, 624-64-6; *cis*-2-butene, 590-18-1.

Effect of a Mercuric Sulfate Precolumn on Chloro Olefin Abstraction[1a]

Donna Nelson,[1b] M. J. S. Dewar,* and J. M. Buschek

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Edward McCarthy*

Allied Chemical Corporation, Morristown, New Jersey 07960

Received April 24, 1979

Use of a mercuric sulfate–sulfuric acid precolumn removes certain chloro olefins but not others. The reason for this difference has been studied. Lack of correlation with π ionization energies, determined by photoelectron spectroscopy combined with MNDO calculations, indicates that attack on the double bonds is not involved. A high correlation with chlorine lone-pair ionization energies, combined with the fact that only allyl chlorides are removed, implies that removal involves mercury-catalyzed solvolysis, a conclusion supported by ^{35}Cl NQR frequencies.

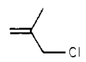
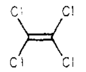
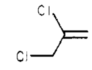
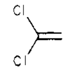
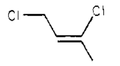
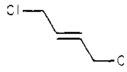
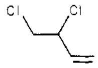
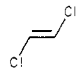
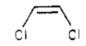
Recently, using a GC/MS technique, we attempted to identify the components of complex reaction mixtures resulting from the chlorofluorination of isobutylene. Most of the components were either four-carbon haloalkanes or haloalkenes. However, it proved difficult to identify the individual components because the fluorochloroalkanes under electron impact gave vanishingly small yields of molecular ions and often fragmented to yield alkene-like mass spectra.[2] It was thought that a precolumn olefin scrubber which would selectively remove unsaturates would greatly assist in the analysis. A comparison of the chromatograms taken with and without the scrubber would then allow GC peaks to be classified as either alkane or alkene.

An olefin scrubbing technique, described some years ago by Francis,[3] was later modified by Innes[4] to meet GC requirements. Innes found that a short precolumn, packed with 20% sulfuric acid impregnated on diatomaceous earth, removed completely the olefin peak from the resulting chromatogram. The olefins ranged from ethylene to 3-heptene.

We therefore constructed a precolumn by packing a short section of Al tubing, 4 in. × $^1/_4$ in. o.d., with 20% mercuric sulfate–20% sulfuric acid loaded on 60/80 mesh Chromosorb P (1 mL of stock solution/g Chromosorb P). The loading was accomplished by rotoevaporating the slurry to dryness. The resulting powder was further dried by heating to 100 °C under vacuum.

This precolumn was, however, found to be generally ineffective in removing F- and Cl-containing olefins from the isobutyl/isobutylene reaction mixtures. The behavior of a number of Cl-containing olefins was therefore studied in the hope of establishing the limitations of this technique.

Table I. Effect of Mercuric Sulfate on Various Chloro Olefins

compd	structure	removal/ nonremoval
I		r
II		nr
III		nr
IV		nr
V[a]		r
VI[b]		r
VII		r
VIII		nr
IX		nr

[a] 4/1 mixture of trans/cis. [b] >95% trans.

For all compounds that were removed by the precolumn, the scrubbing efficiency was 100%; i.e., there was no discernible peak on the chromatogram for a compound that was removed.

The compounds examined, and the effect of the precolumn, are listed in Table I. All of the compounds, with the exception of V, were of greater than 95% purity as determined by GC. All of the compounds gave mass spectra consistent with their structure. Compound V showed two peaks in its chromatogram in the ratio 4/1. NMR showed these peaks to consist of the trans/cis isomer pair. Each of the olefins was examined as a three-compo-

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[1] (a) Presented in part at the National Meeting of the American Chemical Society, Honolulu, Hawaii, Apr. 6, 1979, No. ORGN 487. (b) Robert A. Welch predoctoral fellow.

[2] E. R. McCarthy, unpublished results.

[3] A. W. Francis and S. J. Lukasiewicz, *Ind. Eng. Chem., Anal. Ed.*, 17, 703 (1945).

[4] W. B. Innes, W. E. Bambrick, and A. J. Andreatch, *Anal. Chem.*, 35, 1198 (1963).

0022-3263/79/1944-4109$01.00/0