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Effects of dipolar aprotic solvents and ion pairing on elimination reactions

David Andrew Benko
Union College - Schenectady, NY

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EFFECTS OF DIPOLAR APROTIC SOLVENTS AND ION PAIRING ON ELIMINATION REACTIONS

by David Andrew Benko, UC 1973

Senior Thesis Submitted in Partial Fulfillment of the Requirements for Graduation

DEPARTMENT OF CHEMISTRY
UNION COLLEGE
June, 1973
I wish to thank John R. Sowa under whose direction and understanding this research was conducted.

David A. Benko
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ABSTRACT

An improved method for preparing t-butylacetylene was developed. Starting with t-butyl chloride, aluminum trichloride and vinyl bromide and followed by didehydrohalogenation using potassium hydroxide in dimethyl sulfoxide, t-butylacetylene has been prepared in a better than 70% yield.

In the process the effect of ion pairing on the orientation of elimination reactions was determined. From this a system for converting 2-haloalkanes directly into 2-alkenes was developed.
INTRODUCTION

I. BACKGROUND AND PURPOSE

Although the gross mechanism of base induced elimination reactions have been known for some time, the more intricate details are still under debate. The effects on orientation of base strength, size of base, substituents on the substrate and size of leaving group have been generally accepted for some time. On the other hand, the details concerning ion pairing in the substrate, the timing of the breaking of the C-H and C-halogen bonds are still not understood. In addition, the reason for the cis to trans ratios obtained in these reactions is not really understood. In relatively recent time the effect of protic and dipolar aprotic solvents has been uncovered (1). Even more recently some workers have uncovered the effect of ion pairing involving the base on the relative yields of certain cyclic olefins (2). However no one has looked at the effects of ion pairing on the direction of elimination of simple alkyl halides. This is the subject of one part of the thesis and throws some doubt about the total importance of base strength on orientation in elimination reactions.

A second consideration of the thesis has been the use of dipolar aprotic solvents as a method for the preparation of alkynes as well as the preparation of the dihaloalkanes used
in these preparations. An attempt to prepare di-t-butylacetylene from t-butylacetylene was also made (3).

II. RELEVANT THEORY

A. Alkynes: Alkynes are easily prepared by successive dehydrohalogenation reactions; the first reaction is normally run in an alcoholic solvent using an alkali metal hydroxide, the second, since it involves the breakage of vinyl bonds, uses much more vigorous conditions like sodamide in liquid ammonia (4).

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{CH}_3 - & \quad \text{CH}_3 \\
\text{Cl} & \quad \text{KOH, } 170^\circ \text{C} \\
(\text{HOCH}_2 \text{CH}_2)_2 & \quad \text{O} \\
\text{CH}_3 - & \quad \text{CH}_2 \\
\text{Cl} & \quad \text{NaNH}_3 \\
\text{NH}_3 & \quad \text{(l)} \\
\text{CH}_3 - & \quad \text{C} = \text{CH}
\end{align*}
\]

Actually some didehydrohalogenation occurs in the first step. The more vigorous conditions seem to be required to convert the vinyl halide with the halogen and hydrogen cis to one another (\( \text{H}_2 \text{C} = \text{C} - \text{Cl} \)). Trans dehydrohalogenations are favored over cis eliminations and thus require less energy (5).

It has also been known that apotic solvents such as dimethyl sulfoxide (DMSO), dimethylformamide and acetone can be successfully used as solvents with a number of bases for elimination reactions leading to alkenes (6). Alkoxides are stronger bases in these solvents (probably because of the
lower solvation) and dehydrohalogenations run in these solvents proceed even with bases as weak as bromide ion (7).

The alkoxide/DMSO system was investigated as a means to prepare t-butylacetylene from vinyl halides in a more efficient manner.

B. Alkenes: Dehydrohalogenations of 2-haloalkanes using alkoxides in which DMSO or the corresponding alcohol of the alkoxide is the solvent give both 1- and 2-alkenes (8).

\[
\text{Br} \\
\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 \xrightarrow{\text{base}} \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 + \text{CH}_3\text{CH} = \text{CH}_3 \\
\text{1-alkene} \quad \text{2-alkene}
\]

Orientation in these reactions has been traditionally interpreted as being influenced by (a) base strength, (b) size of base, (c) size of leaving group, (d) degree of branching in the substrate, and (e) stability of the resulting olefin (9).

Saunders states that as base strength increases the amount of 1-olefin also increases. This is illustrated in Table 1.

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influence of Base Strength</td>
</tr>
<tr>
<td>MeO&lt;sup&gt;−&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ratio (2/1)</td>
</tr>
</tbody>
</table>
The relationship between orientation and base size is shown in Table 2.

Table 2

Influence of the Size of the Base

<table>
<thead>
<tr>
<th>Ratio (2/1)</th>
<th>EtO $\supseteq$</th>
<th>t-BuO $\supseteq$</th>
<th>Et$\text{CMe}_3$O $\supseteq$</th>
<th>Et$\text{C}_3$O $\supseteq$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{4}{37}$</td>
<td>.23</td>
<td>.09</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It can be seen that 1-olefin increases as base size increases.

Table 3 shows a similar relationship with size of leaving group and 1-olefin.

Table 3

Influence of the Size of the Leaving Group

<table>
<thead>
<tr>
<th>Ratio (2/1)</th>
<th>-Br</th>
<th>-SMe$_2$ $\supseteq$</th>
<th>-SO$_2$Me</th>
<th>-NMe$_3$ $\supseteq$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td>.15</td>
<td>.13</td>
<td>ca.02</td>
<td></td>
</tr>
</tbody>
</table>

As the degree of branching increases the amount of 1-olefin increases as can been seen in Table 4.
Table 4

Influence of Substituents on the Substrate

<table>
<thead>
<tr>
<th></th>
<th>Ratio (2/1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtCMe₂Br</td>
<td>2.3</td>
</tr>
<tr>
<td>(n-Pr)CMe₂Br</td>
<td>1.0</td>
</tr>
<tr>
<td>(i-Bu)CMe₂Br</td>
<td>.85</td>
</tr>
<tr>
<td>(neo-C₂H₅)CMe₂Br</td>
<td>.16</td>
</tr>
</tbody>
</table>

Generally when stability of the olefin is the determining factor, the 2-olefin will predominate over the 1-olefin.
EXPERIMENTAL

I. PREPARATION OF t-BUTYLACETYLENE

Part A: Preparation of 1-Bromo-1-Chloro-3,3-Dimethylbutane

To a 3-necked 500-ml round bottomed flask equipped with a condenser, addition funnel, thermometer and a teflon coated magnetic stirring bar was added 132 g (1.60 moles) of t-butyl chloride. The flask was cooled to -25°C (0°C can be used with a slight decrease in yield) with a dry ice-acetone bath and 3.00 g of anhydrous aluminum trichloride was added. About 164 g (1.60 moles) of vinyl bromide was poured from a gas cylinder which had been precooled to below 10°C and added slowly to the reaction mixture over a 30-45 minute period while keeping the reaction mixture between -30 to -20°C. The reaction is exothermic and the temperature rises rapidly if the addition of the vinyl bromide is too fast.

After the addition of the vinyl bromide was complete, the reaction mixture was kept between -30 to -25°C for 30 minutes before it was decanted into 50 ml of water and stirred until two colorless phases were present. The organic layer was separated, washed with 50 ml of 10 percent aqueous sodium hydroxide and two 50-ml portions of water before drying overnight over potassium hydroxide.

Yield: 306 g (95.4%). Boiling range: 158-64°C
Part B: Dehydrohalogenation of 1-Bromo-1-Chloro-3,3-Dimethylbutane

1 - Using Potassium Hydroxide: Into a 500-ml 3-necked round bottomed flask equipped with a stirrer, addition funnel, thermometer and 2 condensers (see Figure 1) was added 112 g (2.00 moles) of potassium hydroxide and 250 ml of dimethylsulfoxide. The stirred mixture was heated until the potassium hydroxide melted. The heat was turned off and 100 g (0.50 mole) of 1-bromo-1-chloro-3,3-dimethylbutane was added at such a rate as to maintain a 38-40°C head temperature. After addition was complete, the addition funnel was replaced with a thermometer, the heat turned on and the distillation continued until a pot temperature of 155°C was reached. The t-butylacetylene was then fractionally distilled.

Yield: 30 g (73.2%). Boiling range: 37-9°C

2 - Using Sodium Hydroxide: Proceed as in Part B 1 using 28 g of NaOH in 75 ml DMSO. While 70 ml of 1-chloro-1-bromo-3,3-dimethylbutane was being added, bubbling occurred at 90°C. The product came over at 140°C and 11 ml of t-butylacetylene was recovered.

Yield: (50%, assuming density 1g/ml for t-butylacetylene).
Figure 1

Apparatus for the Preparation of t-Butylacetylene

Condenser 1
(Packed with glass beads)

Condenser 2

Ice bath

Warm water in-temperature: 40-5°C
II. PREPARATION OF VINYL BROMIDE

Into a 3-necked 500-ml round bottomed flask equipped with a stirrer, addition funnel, thermometer, 6-inch Hemple column and 6-inch condenser was added 60 g (1.6 moles) of sodium hydroxide and 125 ml of dimethyl sulfoxide. The stirred mixture was heated to 100°C where 136 ml (1.6 moles) of BrCH₂CH₂Br was added such that the pot temperature remained at 120°C and the head at 65°C. The product was collected in a 100-ml round bottomed flask emersed in a dry ice-acetone bath. About 80 ml of vinyl bromide was recovered (b.p. 16°C).

Yield: (50%).

III. ATTEMPTED CONDENSATION REACTIONS OF ALKYL HALIDES AND t-BUTYLACETYLENE

Attempted Preparation of 2,2,5-Trimethyl-4-hexyne: To a 25-ml round bottomed flask equipped with a condenser, thermometer, magnetic stirring bar was added .1 mole (6.8 g) i-propylacetylene and 5 ml BF₃·OEt which was cooled to 0°C in an ice bath. Approximately .1 mole (9.2 g) of t-butyl chloride was then slowly added such that the temperature remained between 0°C-5°C. The mixture was stirred for 1 hr. at 0°C and for 1 day at room temperature. The starting materials were recovered and the reaction was assumed unsuccessful.
Attempted Preparation of Di-t-Butylacetylene:

a - To a 25-ml round bottomed flask equipped with a condenser, thermometer, a magnetic stirring bar and cooled to -10°C in a dry ice-acetone bath was added .1 mole (9.2 g) t-butyl chloride and 1 g AlCl₃. To the cooled mixture was slowly added .1 mole (8.2 g) t-butylacetylene slowly and the mixture was stirred for 2 hrs. at -10°C and for 1 week at room temperature. This was unsuccessful as the starting materials were recovered.

b - Into an apparatus similar to that in part "a" was added .1 mole (7.4 g) t-butanol, 1 g ZnCl₂ and 1 g HgCl₂ at room temperature. t-Butylacetylene (.1 mole, 8.2 g) was then slowly added with stirring. The resultant mixture was two layered with the top layer showing an NMR similar to a compound such as H⁻ \( \text{C} = \text{CH}_2 \) where X is a t-butyl group. This was thought to be \((\text{CH}_3)_3\text{CCH} = \text{CH}_2\). The bottom layer showed a brood peak at 6.0 and could not be identified. NMR (δ, ppm, neat): 1.3, s(9 H); 5.5, q(1 H); 5.8, q(1 H); 6.2, q(1 H).

c - The procedure was the same as in part "b" except the temperature was kept at 0°C by an ice bath. The results were the same as in "b."

d - Proceed as in part "c" using .1 mole (9.2 g) of t-butyl chloride in place of t-butanol. The results were the same as in "b."
In a test tube was mixed t-butylacetylene, ZnCl₂ and HgCl₂ in the same ratio as "b." The tube was shaken and two layers resulted as in "b" above. This shows that the t-butylacetylene alone is giving the two layers.

IV. PREPARATION OF N,N,N-TRIMETHYLSORBUTYLAMMONIUM IODIDE

To a 3-necked 250-ml round bottomed flask equipped with a condenser, calcium chloride drying tube, thermometer, addition funnel and stirring bar was added 25 ml (.25 mole) secbutylamine and 120 ml acetonitrile. The mixture was heated to 50°C and 50 g (.5 mole) Na₂CO₃ was added. Over a period of 1 hr., 35 ml (.5 mole) of methyliodide was added dropwise with stirring. A temperature rise to 70°C was noted. The mixture was washed with water and N,N-dimethylessorbutylamine resulted.

This product was mixed with 25 g Na₂CO₃ and an additional 15 ml methyliodide was added as before. After washing N,N,N-trimethylessorbutylammonium iodide resulted.

(Sublimation point 260°C)

V. PREPARATION OF 2-BROMOOCTANE (10)

To a 250-ml round bottomed flask was added 50 ml of 2-octanol and 36 ml of 45% hydrobromic acid. The flask was cooled in an ice bath and 15 ml of concentrated sulfuric acid
was slowly added. An additional 2.5 ml of sulfuric acid was added and the mixture stirred for 1/2 hr. The mixture was washed with water and dried over sodium sulfate. 2-Bromobutane (20 g, yield 30%, b.p. 76°C) resulted. Purity was determined by IR, showing the absence of the O-H group.

VI. ELIMINATION REACTIONS

The following general procedure was used when studying the effects on the orientation of elimination reactions. Approximately 20 ml of solvent was put in a 50-ml 1-neck round bottomed flask equipped with a serum cap and a balloon serving as a pressure release device (see Figure 2) and 1 g of base was added to it. The mixture was heated in an oil bath. When the system thermally equilibrated, 1 g of the haloalkane was added with stirring. After the reaction had started, the gaseous alkenes were removed with a syringe and injected into a vapor phase chromatograph. A Perkin-Elmer Model 154 Vapor Fractometer equipped with a 2 meter diisodecyl phthalate column was used. Helium gas was used as a carrier, with a column pressure 10 psi. The column was kept at room temperature. By the cut and weigh method the relative proportions of 1- and 2-olefin were determined.
The following systems were run:

<table>
<thead>
<tr>
<th>System</th>
<th>Ratio (2/1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br + MeO® MeOH 50°C</td>
<td>5.8</td>
</tr>
<tr>
<td>Br + MeO® DMSO 50°C</td>
<td>2.6</td>
</tr>
<tr>
<td>Br + EtO® EtOH 50°C</td>
<td>2.6</td>
</tr>
<tr>
<td>Br + t-BuO® t-BuOH 50°C</td>
<td>1.0</td>
</tr>
<tr>
<td>Br + t-BuOK DMSO 25°C</td>
<td>2.2</td>
</tr>
<tr>
<td>Br + t-BuOK DMSO 50°C</td>
<td>2.4</td>
</tr>
<tr>
<td>Br + KOH DMSO 50°C</td>
<td>2.6</td>
</tr>
<tr>
<td>System</td>
<td>Ratio (2/1)</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>Br + *A-OH [\xrightarrow{\text{DMSO}} 50^\circ C] *Strong base anion exchange resin</td>
<td>5.4</td>
</tr>
<tr>
<td>Br + *A-OH [\xrightarrow{\text{DMSO}} 50^\circ C] All butene-1</td>
<td>10.2</td>
</tr>
<tr>
<td>Br + t-BuOK [\xrightarrow{\text{Ph}_2\text{SO}} 50^\circ C]</td>
<td>1.9</td>
</tr>
<tr>
<td>Br + NEt\textsubscript{3} [\xrightarrow{\text{DMSO}} 50^\circ C]</td>
<td>4.2</td>
</tr>
<tr>
<td>Br + NEt\textsubscript{3} [\xrightarrow{\text{DMSO}} 50^\circ C] All butene-1</td>
<td></td>
</tr>
<tr>
<td>Br + NEt\textsubscript{3} [\xrightarrow{\text{DMSO}} 100^\circ C] 1 hr. - 6.5 1.5 hrs. - 6.6 2 hrs. - 9.2 2.5 hrs. - 12.8</td>
<td></td>
</tr>
<tr>
<td>System</td>
<td>Ratio (2/1)</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>( \text{Br} + 3\text{NEt}_3 \rightarrow \text{DMSO}^{100^\circ C} )</td>
<td>All butene-1</td>
</tr>
<tr>
<td>( \text{Br} + \text{Et}_4\text{NBr} \rightarrow \text{DMSO}^{80^\circ C} )</td>
<td>ca. 10</td>
</tr>
<tr>
<td>( \text{Br} + \text{N}^{2+} \rightarrow \text{DMSO}^{100^\circ C} )</td>
<td>17.3</td>
</tr>
<tr>
<td>( \text{Br} + \text{N}^{4+} \rightarrow \text{DMSO}^{100^\circ C} )</td>
<td>All butene-1</td>
</tr>
<tr>
<td>( \text{Br} + \text{Me}_4\text{N}^{2+} \rightarrow \text{DMSO}^{100^\circ C} )</td>
<td>14.0 → 20.4</td>
</tr>
<tr>
<td>( \text{Br} + \text{Me}_4\text{N}^{4+} \rightarrow \text{DMSO}^{100^\circ C} )</td>
<td>All butene-1</td>
</tr>
</tbody>
</table>
NOTE: The ratio of trimethylpyridine to its hydrobromide was 2:1.
It can be seen that in some cases the ratios were changing. This was due to competition with a substitution reaction and can be overcome by adding the halide after the base-solvent system was heated.

The following reactions were also attempted and gave no reaction in each case:

<table>
<thead>
<tr>
<th>System</th>
<th>Ratio (2/1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-bromooctane $+ \overset{N}{\overset{O}{\text{DMSO}}} \overset{150^\circ C}{\rightarrow}$</td>
<td>All butene-2</td>
</tr>
</tbody>
</table>

- $\overset{\text{Br}}{\text{Br}} + \overset{\text{NaOH}}{\overset{\text{t-BuOH}}{\overset{80^\circ C}{\rightarrow}}}$
- $\overset{\text{Br}}{\text{Br}} + \overset{\text{LiOH}}{\overset{\text{DMSO}}{\overset{100^\circ C}{\rightarrow}}}$
- $\overset{\text{Br}}{\text{Br}} + \overset{\text{NaOH}}{\overset{\text{DMSO}}{\overset{90^\circ C}{\rightarrow}}}$
- $\overset{\text{N}}{\overset{\text{Me}}{\overset{\text{Me}}{\overset{\text{Me}}{\overset{\text{DMSO}}{\overset{110^\circ C}{\rightarrow}}}}}}$
The following reactions were analyzed using a 2 meter silicon grease column. In each case the system was saturated with t-BuOK and Dibenzo-18-Crown-16 ether.

<table>
<thead>
<tr>
<th>System</th>
<th>Ratio (2/1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Br} + \text{t-BuOK} \rightarrow \text{DMSO}, 50^\circ \text{C} )</td>
<td>2.1</td>
</tr>
<tr>
<td>( \text{Br} + \text{t-BuOK} \rightarrow \text{DMSO, 50^\circ C}, \text{Crown Ether} )</td>
<td>2.4</td>
</tr>
</tbody>
</table>
Figure 2

Elimination Reaction Apparatus

- Balloon
- Serum Cap
VII. ELIMINATIONS USING SODIUM ETHOXIDE IN ETHANOL

Solutions of sodium ethoxide in ethanol were prepared by adding sodium metal to absolute ethanol such that the concentrations ranged from 0.2M to 1.07M. In each case the ethoxide concentration was 20 times in excess the 2-bromobutane added to the solution.

The solutions were prepared in a 500-ml 1-neck round bottomed flask and were heated to 50°C in a water bath. The 2-bromobutane was added and the resultant olefins were analyzed by G.L.C. as described in the experimental section on "Elimination Reactions." In each case the 2 meter diisodecyl phthalate column was used. The data is presented in Table 5.

Table 5

Data from Ethoxide Eliminations

<table>
<thead>
<tr>
<th>Concentration of Sodium Ethoxide (M)</th>
<th>Vol. of Soln.(ml)</th>
<th>2-Bromo-butane (ml)</th>
<th>Ratio (2/1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>.21</td>
<td>437</td>
<td>.5</td>
<td>2.6</td>
</tr>
<tr>
<td>.40</td>
<td>231</td>
<td>.5</td>
<td>3.0</td>
</tr>
<tr>
<td>.78</td>
<td>264</td>
<td>.5</td>
<td>2.7</td>
</tr>
<tr>
<td>.90</td>
<td>205</td>
<td>1.0</td>
<td>2.5</td>
</tr>
<tr>
<td>1.07</td>
<td>230</td>
<td>1.0</td>
<td>2.6</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

I. The Preparation of t-Butylacetylene: The traditional method of preparation of t-butylacetylene (11) involves the halogenation of pinacolone with phosphorus pentachloride followed by dehydrohalogenation with potassium hydroxide in ethanol. This is illustrated in Figure 3.

Figure 3

Traditional Method of Preparation of t-Butylacetylene

\[
\begin{align*}
\text{CH}_3\text{-C-CH}_3 + \text{Mg} & \rightarrow (\text{CH}_3)_2\text{C-C(CH}_3)_2 + \text{H}^+ \rightarrow (\text{CH}_3)_3\text{C-C-CH}_3 \\
(\text{CH}_3)_3\text{C-CH} & \xrightarrow{\text{KOH}} (\text{CH}_3)_3\text{CCl}_2\text{CH}_3
\end{align*}
\]

This scheme takes up to 17 hours and gives an overall yield of t-butylacetylene of about 20%. It can be seen that the overall efficiency of this method is low.

In this study t-butylacetylene was prepared rather easily in just two steps. The first involves the preparation of a dihalide from t-butyl chloride, aluminum trichloride and vinyl bromide. The second is a one step dehydrohalogenation of this dihalide using KOH in DMSO.
If the DMSO is dry, the elimination step will exotherm at 90°C. On the other hand, the exotherm may occur as high as 130°C if moisture is present.

This two step scheme takes 4-5 hrs. and gives an overall yield of 70%-80%. Comparing this to the conventional method (16 hrs. 20% yield) it can be seen that this is a much more efficient process. The starting materials are easy to obtain and the dihalide is conveniently dehydrohalogenated in one step. The first step can also be run at 0°C with a slight sacrifice in overall yield.

Using similar techniques Sowa (12) has also prepared dimethylacetylene, diphenylacetylene, 2-decyne and 3-methyl-1-butyne. This demonstrates the versatility of this technique since these were prepared from both germinal and vicinal dihalides and were both volatile and non-volatile under reaction conditions. In all cases the reaction times were at least one-third the previous times and the yields were as good or better than the previous methods.
II. Effects of Ion Pairing: From Table 6 it can be seen that base strength plays an important role in product orientation for the bases in alcoholic solvents. In this Table base strength is given by $\text{t-BuO} > \text{EtO} > \text{MeO}$. It can be seen that 2/1 ratios decrease as base strength increases.

Table 6

<table>
<thead>
<tr>
<th>System</th>
<th>Ratio (2/1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeO $/$MeOH</td>
<td>5.8</td>
</tr>
<tr>
<td>MeO $/$DMSO</td>
<td>2.6</td>
</tr>
<tr>
<td>EtO $/$EtOH</td>
<td>2.6</td>
</tr>
<tr>
<td>t-BuO $/$t-BuOH</td>
<td>1.0</td>
</tr>
<tr>
<td>t-BuO $/$DMSO</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Methoxide gives relatively more 1-olefin when going from the protic to dipolar aprotic solvent. This is expected since in DMSO the methoxide ion is less solvated and is therefore a stronger base; the stronger the base the more 1-alkene. Such a decrease is not observed for the t-butoxide ion. Bartsch (8) has explained this as being due to a highly solvated and very hindered alkoxide ion in the alcoholic solvent leading to substantially more 1-alkene than normally expected. If this were truly the case, then the heterogenous reaction in-
volving KOH pellets in DMSO should present an even more hindered surface and might be a possible route to the preparation of 1-alkenes directly from 2-haloalkanes. Since in these reactions there is a color change on the surface of the KOH pellets and the pellets bubble up to form a crust as the reaction proceeds, it was considered that the reactions were taking place on the KOH surface.

Table 7 shows the ratios obtained for this KOH/DMSO system and for a strong base anion exchange resin in DMSO system.

Table 7

<table>
<thead>
<tr>
<th>System</th>
<th>Ratio (2/1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH/DMSO</td>
<td>2.6</td>
</tr>
<tr>
<td>A-OH/DMSO</td>
<td>5.4</td>
</tr>
</tbody>
</table>

The ratio in KOH/DMSO is much higher than expected if hinderance were the factor. In the A-OH/DMSO system the hydroxide ions are expected to be more free and therefore in a high concentration. This system demonstrates that the KOH/DMSO reaction is not just peculiar to the hydroxide ion since its ratio is much higher than the KOH/DMSO ratio. The reaction might still be occurring on the KOH surface but some other factor could also be involved.
From Table 6 a discrepancy in the base strength theory is evident. The fact that t-BuO /DMSO is a much stronger base than MeO /DMSO would lead to a prediction of a large change in 2/1 ratios between the two. The data shows there is very little difference. There must be some other factor influencing orientation.

Closer examination of the data indicates that ion pairing of the base might be a factor. For example, MeO /DMSO appears to be more ion paired than t-BuO /DMSO since it is less soluble.

Table 8 presents some more data to support this evidence.

Table 8

<table>
<thead>
<tr>
<th>System</th>
<th>Ratio (2/1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Benzenoate/DMSO</td>
<td>10.2</td>
</tr>
<tr>
<td>t-BuO /DMSO</td>
<td>2.4</td>
</tr>
<tr>
<td>t-BuO /Ph₂SO</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Sodium benzoate is a weak base and should dissociate to a greater extent in DMSO than alkoxides of low molecular alcohols. The 10.2 ratio is consistent with this prediction.

Diphenyl sulfoxide has a lower dielectric constant than DMSO (13, 14) and potassium t-butoxide should be less dissociated in it than in DMSO. This also eliminates the dimethyl
ion as being the base since \( \text{Ph}_2\text{SO} \) has no \( \alpha \)-hydrogens. The fact that \( \text{t}-\text{BuO}^+ / \text{Ph}_2\text{SO} \) is more ion paired than \( \text{t}-\text{BuO}^- / \text{DMSO} \) and that each have different ratios supports the ion pairing proposition; the more ion pairing the relatively more 1-olefin formed.

Table 9 presents data in which no ion pairing is present in the base.

Table 9

<table>
<thead>
<tr>
<th>System (°C)</th>
<th>Ratio (2/1)</th>
<th>PK</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NEt}_3 / \text{DMSO} (100°C) )</td>
<td>12.8</td>
<td>11.0</td>
</tr>
<tr>
<td>( \text{Et}_4\text{NBr} / \text{DMSO} (80°C) )</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>( \text{Pyridine} / \text{DMSO} (100°C) )</td>
<td>17.3</td>
<td>5.2</td>
</tr>
<tr>
<td>( 2,4,6\text{-Trimethylpyridine} / \text{DMSO} (100°C) )</td>
<td>17.3</td>
<td>9.6</td>
</tr>
<tr>
<td>( 2,4,6\text{-Trimethylpyridine} / 2,4,6\text{-Trimethylpyridine hydrobromide} / \text{DMSO} (150°C) )</td>
<td>32.2</td>
<td></td>
</tr>
</tbody>
</table>

These all show ratios which are high in 2-olefin. This is expected since there are no ion pairs. The \( 2,4,6\text{-Trimethylpyridine} / \text{DMSO} \) system possesses a base which is very hindered (as much as \( \text{t}-\text{BuO}^- \)) and which is a stronger base than pyridine. However it gives a ratio as high as that for pyridine and much higher than that for \( \text{t}-\text{BuO}^- / \text{DMSO} \). This would not be expected if steric factors or base strength
determined the orientation. It does support the ion pair theory however.

By using a system with 2,4,6-trimethylpyridine with its hydrobromide in DMSO a ratio of 32.1:1 or a purity of greater than 97% 2-olefin was obtained. This is obviously a useful synthetic method for the preparation of 2-olefins.

III. Crown Ethers: Table 10 shows some data obtained when a silicon grease column was used with t-BuOK reactions.

Table 10

t-BuOK/DMSO Systems

<table>
<thead>
<tr>
<th>System</th>
<th>Ratio (2/1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-BuOK/DMSO</td>
<td>2.1</td>
</tr>
<tr>
<td>t-BuOK/Crown Ether/DMSO</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Crown ethers tend to pull apart ion pairs by solvating the cation (15). It can be assumed that there is less ion pairing in the crown ether system and the ratio would be expected to be higher. From the Table this is seen to be the case.

Sowa (12) performed the experiments in Table 11. This Table shows how the 2/1 ratios changed when "Johnson's Baby Shampoo" or when crown ether was added to the systems.
Table 11

Shampoo and Crown Ether Systems

<table>
<thead>
<tr>
<th>System</th>
<th>2/1 Ratio Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtO⁻/EtOH/Shampoo</td>
<td>no change</td>
</tr>
<tr>
<td>EtO⁻/EtOH/Crown Ether</td>
<td>no change</td>
</tr>
<tr>
<td>MeO⁻/DMSO/Shampoo</td>
<td>increase</td>
</tr>
<tr>
<td>t-BuO⁻/DMSO/Shampoo</td>
<td>increase</td>
</tr>
</tbody>
</table>

The shampoo is thought to be similar to the crown ether in its solvating properties. The MeO⁻ and t-BuO⁻ systems show the expected increase in 2-olefin with the decreased ion pairing. However, the ethoxide ion shows no change in either case. Some possible reasons for this are that the ions are bound tighter in EtOH and cannot be pulled apart as easily or that the protons are negating the effect of the shampoo or crown ether.

Table 5 shows another peculiarity of the ethanol system. There is a very slight ratio change for each concentration. It would be expected that ion pairs would increase with concentration. This is not the case and perhaps the same reasoning can be followed here as in the crown ether cases.

In the reactions presented, rearrangement of the double bond was ruled out by running reactions with 1-bromobutane. Since no 2-butene was observed, rearrangement was ruled out.
IV. Summary: A method has been developed for preparing t-butylacetylene by two rather simple reactions. The effect of ion pairs on the orientation of the double bond in elimination reactions has been determined. Finally, a method for preparing rather pure 2-alkenes from 2-haloalkanes has been found where previous methods usually did not give much better than an 8:1 ratio of the 2- to 1-alkenes.
THE NEXT STEP

Since ion pairs are being dealt with, further work should be carried out to determine exactly what type of pairs are involved. One type could react much differently than another type. A study of this nature might also shed some light on the peculiarities of the ethanol systems.

It would also be helpful to have some kinetic data on these reactions. If one type of ion pair reacts faster than another, some kinetic information would help determine this.

Some changes in the cis to trans ratio were observed in some of these studies. The cis/trans ratios of the 2-olefin should therefore be looked at closer. This could provide useful information relating to the mechanism of these reactions.

Reactions with crown ethers in the system should also be continued to further verify the theory presented.

Finally, the attempts to condense alkyl halides with t-butylacetylene should be studied more carefully.
BIBLIOGRAPHY